

## Chapter 15

### Applying equilibrium

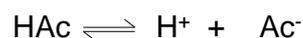
### The Common Ion Effect

- When the salt with the anion of a weak acid is added to that acid,
- It reverses the dissociation of the acid.
- Lowers the percent dissociation of the acid.
- The same principle applies to salts with the cation of a weak base.
- The calculations are the same as last chapter.

### Buffered solutions

- A solution that resists a change in pH.
- Either a weak acid and its salt or a weak base and its salt.
- We can make a buffer of any pH by varying the concentrations of these solutions.
- Same calculations as before.
- Calculate the pH of a solution that is .50 M HAc and .25 M NaAc ( $K_a = 1.8 \times 10^{-5}$ )

$\text{Na}^+$  is a spectator and the reaction we are worried about is



Initial	0.50 M	0	0.25 M
$\Delta$	-x	x	x
Final	0.50-x	x	0.25+x

- Choose x to be small
- We can fill in the table

	$\text{HAc}$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{Ac}^-$
Initial	0.50 M		0		0.25 M
$\Delta$	-x		x		x
Final	0.50-x		x		0.25+x

- Do the math

- $K_a = 1.8 \times 10^{-5}$

$$1.8 \times 10^{-5} = \frac{x(0.25+x)}{(0.50-x)} = \frac{x(0.25)}{(0.50)}$$

- Assume x is small

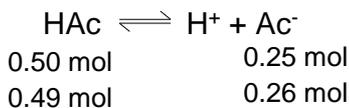
- Assumption is valid

- $\text{pH} = -\log(3.6 \times 10^{-5}) = 4.44$

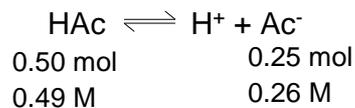
$$x = 3.6 \times 10^{-5}$$

### Adding a strong acid or base

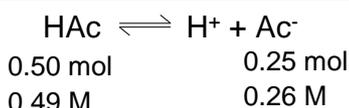
- Do the stoichiometry first.
  - Use moles not molar
- A strong base will grab protons from the weak acid reducing  $[\text{HA}]_0$
- A strong acid will add its proton to the anion of the salt reducing  $[\text{A}^-]_0$
- Then do the equilibrium problem.
- What is the pH of 1.0 L of the previous solution when 0.010 mol of solid NaOH is added?



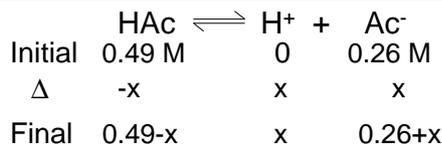
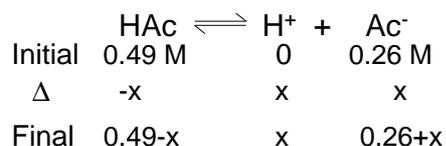
- In the initial mixture  $M \times L = \text{mol}$
- $0.50 \text{ M HAc} \times 1.0 \text{ L} = 0.50 \text{ mol HAc}$
- $0.25 \text{ M Ac}^- \times 1.0 \text{ L} = 0.25 \text{ mol Ac}^-$
- Adding  $0.010 \text{ mol OH}^-$  will reduce the HAc and increase the  $\text{Ac}^-$  by  $0.010 \text{ mole}$
- Because it is in  $1.0 \text{ L}$ , we can convert it to molarity



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- Fill in the table



- Do the math
- $K_a = 1.8 \times 10^{-5}$
- $$1.8 \times 10^{-5} = \frac{x(0.26+x)}{(0.49-x)} = \frac{x(0.26)}{(0.49)}$$
- Assume  $x$  is small
- Assumption is valid  $x = 3.4 \times 10^{-5}$
- $\text{pH} = -\log(3.4 \times 10^{-5}) = 4.47$

### Notice

- If we had added  $0.010 \text{ mol}$  of  $\text{NaOH}$  to  $1 \text{ L}$  of water, the  $\text{pH}$  would have been.
- $0.010 \text{ M OH}^-$
- $\text{pOH} = 2$
- $\text{pH} = 12$
- But with a mixture of an acid and its conjugate base the  $\text{pH}$  doesn't change much
- Called a buffer.

### General equation

- $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
- so  $[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$
- The  $[\text{H}^+]$  depends on the ratio  $[\text{HA}]/[\text{A}^-]$
- taking the negative log of both sides
- $\text{pH} = -\log(K_a [\text{HA}]/[\text{A}^-])$
- $\text{pH} = -\log(K_a) - \log([\text{HA}]/[\text{A}^-])$
- $\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$

### This is called the Henderson-Hasselbach equation

- $\text{pH} = \text{pKa} + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
- $\text{pH} = \text{pKa} + \log(\text{base/acid})$
- Works for an acid and its salt
- Like  $\text{HNO}_2$  and  $\text{NaNO}_2$
- Or a base and its salt
- Like  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$
- But remember to change  $K_b$  to  $K_a$

- Calculate the pH of the following
- 0.75 M lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) and 0.25 M sodium lactate ( $K_a = 1.4 \times 10^{-4}$ )

•  $\text{pH} = 3.38$

- Calculate the pH of the following
- 0.25 M  $\text{NH}_3$  and 0.40 M  $\text{NH}_4\text{Cl}$  ( $K_b = 1.8 \times 10^{-5}$ )
- $K_a = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$
- $K_a = 5.6 \times 10^{-10}$
- remember its the ratio base over acid

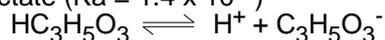
•  $\text{pH} = 9.05$

### Prove they're buffers

- What would the pH be if .020 mol of HCl is added to 1.0 L of both of the preceding solutions.
- What would the pH be if 0.050 mol of solid NaOH is added to 1.0 L of each of the proceeding.
- Remember adding acids increases the acid side,
- Adding base increases the base side.

### Prove they're buffers

- What would the pH be if .020 mol of HCl is added to 1.0 L of preceding solutions.
- 0.75 M lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) and 0.25 M sodium lactate ( $K_a = 1.4 \times 10^{-4}$ )

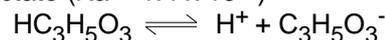


Initially	0.75 mol	0	0.25 mol
After acid	0.77 mol		0.23 mol

Compared to 3.38 before acid was added

### Prove they're buffers

- What would the pH be if 0.050 mol of solid NaOH is added to 1.0 L of the solutions.
- 0.75 M lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) and 0.25 M sodium lactate ( $K_a = 1.4 \times 10^{-4}$ )



Initially	0.75 mol	0	0.25 mol
After acid	0.70 mol		0.30 mol

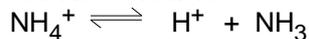
Compared to 3.38 before acid was added

### Prove they're buffers

- What would the pH be if .020 mol of HCl is added to 1.0 L of preceding solutions.

- 0.25 M  $\text{NH}_3$  and 0.40 M  $\text{NH}_4\text{Cl}$

$$K_b = 1.8 \times 10^{-5} \text{ so } K_a = 5.6 \times 10^{-10}$$



Initially	0.40 mol	0	0.25 mol
After acid	0.42 mol		0.23 mol

Compared to 9.05 before acid was added

### Prove they're buffers

- What would the pH be if 0.050 mol of solid NaOH is added to 1.0 L each solutions.

- 0.25 M  $\text{NH}_3$  and 0.40 M  $\text{NH}_4\text{Cl}$

$$K_b = 1.8 \times 10^{-5} \text{ so } K_a = 5.6 \times 10^{-10}$$



Initially	0.40 mol	0	0.25 mol
After acid	0.35 mol		0.30 mol

Compared to 9.05 before acid was added

### Buffer capacity

- The pH of a buffered solution is determined by the ratio  $[\text{A}^-]/[\text{HA}]$ .
- As long as this doesn't change much the pH won't change much.
- The more concentrated these two are the more  $\text{H}^+$  and  $\text{OH}^-$  the solution will be able to absorb.
- Larger concentrations = bigger buffer capacity.

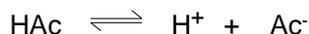
### Buffer Capacity

- Calculate the change in pH that occurs when 0.020 mol of HCl(g) is added to 1.0 L of each of the following:
  - 5.00 M HAc and 5.00 M NaAc
  - 0.050 M HAc and 0.050 M NaAc
  - $K_a = 1.8 \times 10^{-5}$
- $\text{pH} = \text{p}K_a$

### Buffer Capacity

- Calculate the change in pH that occurs when 0.040 mol of HCl(g) is added to 1.0 L of 5.00 M HAc and 5.00 M NaAc

- $K_a = 1.8 \times 10^{-5}$



Initially	5.00 mol	0	5.00 mol
After acid	5.04 mol		4.96 mol

Compared to 4.74 before acid was added

### Buffer Capacity

- Calculate the change in pH that occurs when 0.040 mol of HCl(g) is added to 1.0 L of 0.050 M HAc and 0.050 M NaAc

- $K_a = 1.8 \times 10^{-5}$



Initially	0.050 mol	0	0.050 mol
After acid	0.090 mol	0	0.010 mol

Compared to 4.74 before acid was added

## Buffer capacity

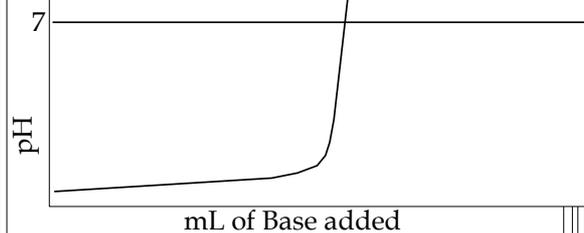
- The best buffers have a ratio  $[A^-]/[HA] = 1$
- This is most resistant to change
- True when  $[A^-] = [HA]$
- Makes  $pH = pKa$  (since  $\log 1 = 0$ )

## Titrations

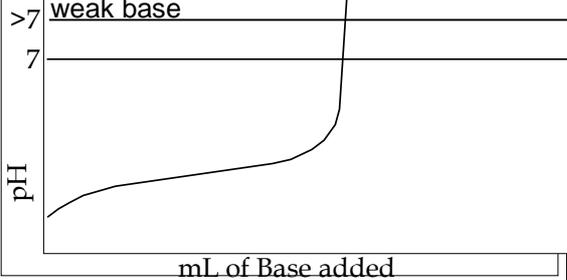
- Millimole (mmol) = 1/1000 mol
- Molarity = mmol/mL = mol/L
- Makes calculations easier because we will rarely add liters of solution.
- Adding a solution of known concentration until the substance being tested is consumed.
- This is called the equivalence point.
- Graph of pH vs. mL is a titration curve.

## Titration Curves

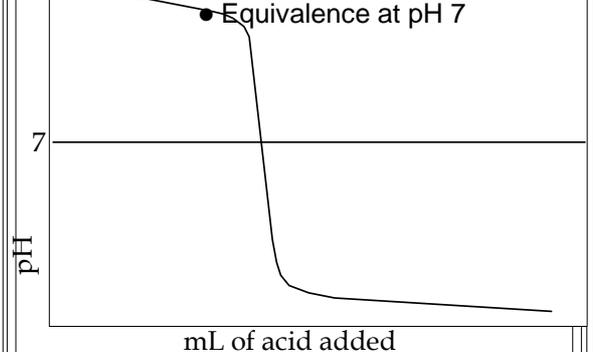
- Strong acid with strong Base
- Equivalence at pH 7

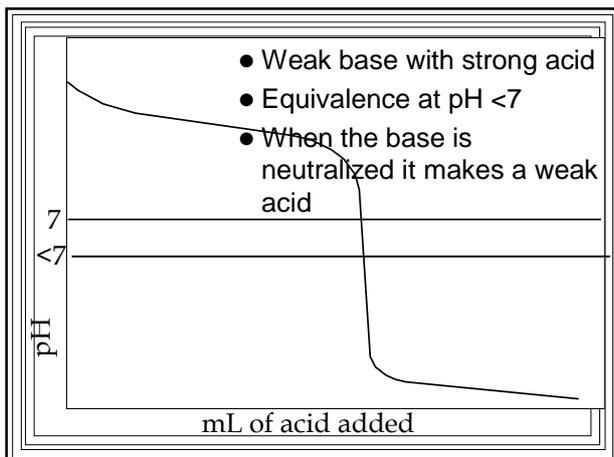


- Weak acid with strong Base
- Equivalence at  $pH > 7$
- When the acid is neutralized it makes a weak base



- Strong base with strong acid
- Equivalence at pH 7





### Strong acid with Strong Base

- Do the stoichiometry.
- $mL \times M = mmol$
- There is no equilibrium .
- They both dissociate completely.
- The reaction is  $H^+ + OH^- \rightarrow HOH$
- Use  $[H^+]$  or  $[OH^-]$  to figure pH or pOH
- The titration of 50.0 mL of 0.200 M  $HNO_3$  with 0.100 M NaOH

### Weak acid with Strong base

- There is an equilibrium.
- Do stoichiometry.
  - Use moles
- Determine major species
- Then do equilibrium.
- Titrate 50.0 mL of 0.10 M HF ( $K_a = 7.2 \times 10^{-4}$ ) with 0.10 M NaOH

### Summary

- Strong acid and base just stoichiometry.
- Weak acid with 0 ml of base -  $K_a$
- Weak acid before equivalence point
  - Stoichiometry first
  - Then Henderson-Hasselbach
- Weak acid at equivalence point-  $K_b$ 
  - Calculate concentration
- Weak acid after equivalence - leftover strong base.
  - Calculate concentration

### Summary

- Weak base before equivalence point.
  - Stoichiometry first
  - Then Henderson-Hasselbach
- Weak base at equivalence point  $K_a$ .
  - Calculate concentration
- Weak base after equivalence – left over strong acid.
  - Calculate concentration

### Indicators

- Weak acids that change color when they become bases.
- weak acid written  $HIn$
- Weak base
- $HIn \rightleftharpoons H^+ + In^-$   
 clear                      red
- Equilibrium is controlled by pH
- End point - when the indicator changes color.
- Try to match the equivalence point

### Indicators

- Since it is an equilibrium the color change is gradual.
- It is noticeable when the ratio of  $[In^-]/[HI]$  or  $[HI]/[In^-]$  is 1/10
- Since the Indicator is a weak acid, it has a  $K_a$ .
- pH the indicator changes at is.
- $pH=pK_a + \log([In^-]/[HI]) = pK_a + \log(1/10)$
- $pH=pK_a - 1$  on the way up

### Indicators

- $pH=pK_a + \log([HI]/[In^-]) = pK_a + \log(10)$
- $pH=pK_a+1$  on the way down
- Choose the indicator with a  $pK_a$  1 more than the pH at equivalence point if you are titrating with base.
- Choose the indicator with a  $pK_a$  1 less than the pH at equivalence point if you are titrating with acid.

### Solubility Equilibria

Will it all dissolve, and if not, how much?

- All dissolving is an equilibrium.
- If there is not much solid it will all dissolve.
- As more solid is added the solution will become saturated.
- Solid  $\rightleftharpoons$  dissolved
- The solid will precipitate as fast as it dissolves .
- Equilibrium

### General equation

- $M^+$  stands for the cation (usually metal).
- $Nm^-$  stands for the anion (a nonmetal).
- $M_aNm_b(s) \rightleftharpoons aM^+(aq) + bNm^-(aq)$
- $K = [M^+]^a[Nm^-]^b/[M_aNm_b]$
- But the concentration of a solid doesn't change.
- $K_{sp} = [M^+]^a[Nm^-]^b$
- Called the solubility product for each compound.

### Watch out

- Solubility is not the same as solubility product.
- Solubility product is an equilibrium constant.
- it doesn't change except with temperature.
- Solubility is an equilibrium position for how much can dissolve.
- A common ion can change this.

### Calculating $K_{sp}$

- The solubility of iron(II) oxalate  $FeC_2O_4$  is 65.9 mg/L
- The solubility of  $Li_2CO_3$  is 5.48 g/L

### Calculating Solubility

- The solubility is determined by equilibrium.
- Its an equilibrium problem.
- Watch the coefficients
- Calculate the solubility of  $SrSO_4$ , with a  $K_{sp}$  of  $3.2 \times 10^{-7}$  in M and g/L.
- Calculate the solubility of  $Ag_2CrO_4$ , with a  $K_{sp}$  of  $9.0 \times 10^{-12}$  in M and g/L.

### Relative solubilities

- $K_{sp}$  will only allow us to compare the solubility of solids that fall apart into the same number of ions.
- The bigger the  $K_{sp}$  of those the more soluble.
- If they fall apart into different number of pieces you have to do the math.

### Common Ion Effect

- If we try to dissolve the solid in a solution with either the cation or anion already present less will dissolve.
- Calculate the solubility of  $SrSO_4$ , with a  $K_{sp}$  of  $3.2 \times 10^{-7}$  in M and g/L in a solution of 0.010 M  $Na_2SO_4$ .
- Calculate the solubility of  $SrSO_4$ , with a  $K_{sp}$  of  $3.2 \times 10^{-7}$  in M and g/L in a solution of 0.010 M  $SrNO_3$ .

### pH and solubility

- $OH^-$  can be a common ion.
- More soluble in acid.
- For other anions if they come from a weak acid they are more soluble in a acidic solution than in water.
- $CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2}$
- $H^+ + C_2O_4^{-2} \rightleftharpoons HC_2O_4^-$
- Reduces  $[C_2O_4^{-2}]$  in acidic solution.

### Precipitation

- Ion Product,  $Q = [M^+]^a[Nm^-]^b$
- If  $Q > K_{sp}$  a precipitate forms.
- If  $Q < K_{sp}$  No precipitate.
- If  $Q = K_{sp}$  equilibrium.
- A solution of 750.0 mL of  $4.00 \times 10^{-3}M$   $Ce(NO_3)_3$  is added to 300.0 mL of  $2.00 \times 10^{-2}M$   $KIO_3$ . Will  $Ce(IO_3)_3$  ( $K_{sp} = 1.9 \times 10^{-10}M$ ) precipitate and if so, what is the concentration of the ions?

### Selective Precipitations

- Used to separate mixtures of metal ions in solutions.
- Add anions that will only precipitate certain metals at a time.
- Used to purify mixtures.
- Often use  $H_2S$  because in acidic solution  $Hg^{+2}$ ,  $Cd^{+2}$ ,  $Bi^{+3}$ ,  $Cu^{+2}$ ,  $Sn^{+4}$  will precipitate.

### Selective Precipitation

- Then add  $OH^-$  solution  $[S^{-2}]$  will increase so more soluble sulfides will precipitate.
- $Co^{+2}$ ,  $Zn^{+2}$ ,  $Mn^{+2}$ ,  $Ni^{+2}$ ,  $Fe^{+2}$ ,  $Cr(OH)_3$ ,  $Al(OH)_3$

### Selective precipitation

- Follow the steps
- First with insoluble chlorides (Ag, Pb, Ba)
- Then sulfides in Acid.
- Then sulfides in base.
- Then insoluble carbonate (Ca, Ba, Mg)
- Alkali metals and  $NH_4^+$  remain in solution.

### Complex ion Equilibria

- A charged ion surrounded by ligands.
- Ligands are Lewis bases using their lone pair to stabilize the charged metal ions.
- Common ligands are  $NH_3$ ,  $H_2O$ ,  $Cl^-$ ,  $CN^-$
- Coordination number is the number of attached ligands.
- $Cu(NH_3)_4^{2+}$  has a coordination # of 4

### The addition of each ligand has its own equilibrium

- Usually the ligand is in large excess.
- And the individual  $K$ 's will be large so we can treat them as if they go to completion.
- The complex ion will be the biggest ion in solution.

- Calculate the concentrations of  $Ag^+$ ,  $Ag(S_2O_3)^-$ , and  $Ag(S_2O_3)_2^{-3}$  in a solution made by mixing 150.0 mL of 0.010 M  $AgNO_3$  with 200.0 mL of 5.00 M  $Na_2S_2O_3$
- $Ag^+ + S_2O_3^{-2} \rightleftharpoons Ag(S_2O_3)^-$   
 $K_1 = 7.4 \times 10^8$
- $Ag(S_2O_3)^- + S_2O_3^{-2} \rightleftharpoons Ag(S_2O_3)_2^{-3}$   
 $K_2 = 3.9 \times 10^4$