

CHEMISTRY 1102 NOTES

ZUMDAHL CHAPTER 15 - APPLICATIONS OF AQUEOUS EQUILIBRIA

The introduction refers to the formation of stalactites and stalagmites as an example of the material in this chapter:

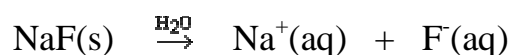


(It is not obvious how this is an example of equilibria involving complexes beyond the use of the "(aq)" in the chemical equations!

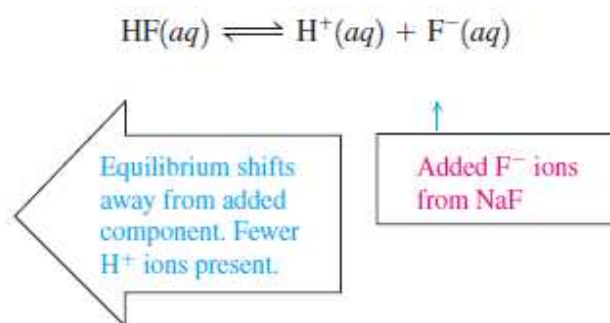
Acid and Base Equilibria

1. Solutions of Acids or Bases Containing a Common Ion

(This is an introduction to the concept of *buffers*.) The example is a solution containing both sodium fluoride and hydrofluoric acid. The sodium fluoride is completely dissociated:



The HF equilibrium is shifted according to the Le Chatelier Principle towards the undissociated acid side:



Another example, this time involving a base, is ammonium chloride added to "ammonium hydroxide" solution:



and this causes the position of the ammonia–water equilibrium to shift to the left:



The effect is called the *common ion effect* and illustrates how an equilibrium does not discriminate between species of different origins. This suggests how to handle the calculations:

Equilibrium Calculations

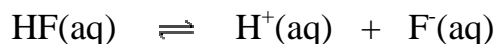
Example: (15.1)

The equilibrium concentration of H^+ in 1.0 M HF is 2.7×10^{-2} M and the percent dissociation of HF is 2.7%. What are the new values if the solution is also 1.0 M in NaF? $K_a = 7.2 \times 10^{-4}$.

Answer:

Major solution species are: HF, F^- , Na^+ and H_2O .

The only active equilibrium equation is:



and:

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4}$$

Starting concentrations:

$$[\text{H}^+] = 0$$

$$[\text{F}^-] = 1.0 \text{ M from NaF which is completely dissociated}$$

$$[\text{HF}] = 1.0 \text{ M}$$

At equilibrium, the concentrations are:

$$[\text{H}^+] = A$$

$$[\text{F}^-] = 1.0 + A \text{ M from NaF which is completely dissociated}$$

$$[\text{HF}] = 1.0 - A \text{ M}$$

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HF}]_0 = 1.0$ (from dissolved HF)	x mol/L HF dissociates \rightarrow	$[\text{HF}] = 1.0 - x$
$[\text{F}^-]_0 = 1.0$ (from dissolved NaF)		$[\text{F}^-] = 1.0 + x$
$[\text{H}^+]_0 = 0$ (neglect contribution from H_2O)		$[\text{H}^+] = x$

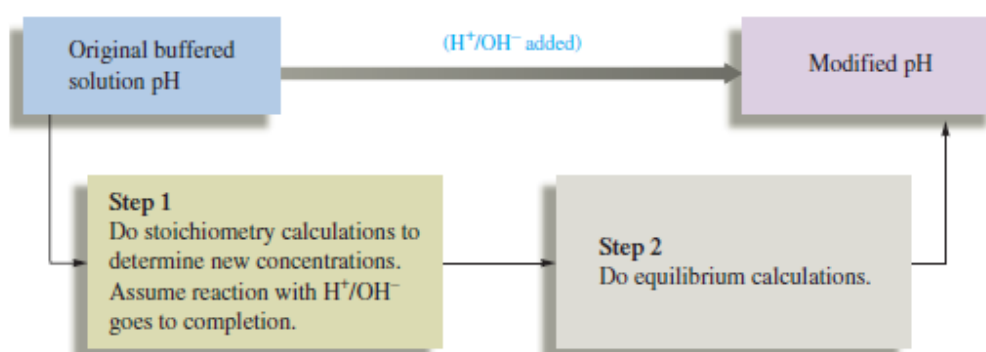
Plug them into the expression for K_a and solve for A making the usual approximation that A is very small compared to 1.0:

$$7.2 \times 10^{-4} = (A)(1.0 + A)/(1.0 - A) \sim A$$

$$\text{The percent dissociation} = [\text{H}^+]/[\text{HF}]_0 = (7.2 \times 10^{-4}/1.0) \times 100\% = 0.072\%$$

2. Buffered Solutions

A buffered solution contains a combination of a weak acid or base and its salt which tends to resist changes to its pH. Buffered solutions are present in all biochemical systems, and are used extensively in the laboratory to control the pH of solutions near to a desired value.



(Exercise 15.2)

A buffered solution is made up to contain 0.50 M acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.50 M sodium acetate. What is its pH?

Answer:

This calculation is exactly analogous to the preceding calculation:

Start:

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.50 \text{ M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.50 \text{ M}$$

$$[\text{H}^+] = 0$$

Equilibrium:

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.50 - A \text{ M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.50 + A \text{ M}$$

$$[\text{H}^+] = A \text{ M}$$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(A)(0.5 + A)}{(0.50 - A)}$$

$$\text{so } A = 1.8 \times 10^{-5}$$

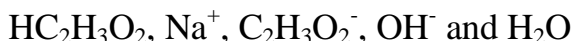
$$\text{and pH} = 4.74$$

i.e. a somewhat acid solution. The interesting thing is to see what happens if, for example (Exercise 15.3)

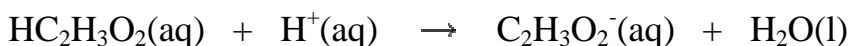
0.01 mol of solid NaOH is added to a litre of this solution:

Answer:

Hypothetically, before any reaction occurs, the major solution species are:



The hydroxide ion present is a strong base and will react with the best source of protons (strongest acid) present, i.e. the acetic acid. This reaction can be treated as being essentially stoichiometric:



The concentration of acetic acid would go from 0.50 M (0.50 mol in 1.0 L) to $0.50 - 0.01 = 0.49 \text{ M}$, and the concentration of acetate will go from 0.50 to $0.50 + 0.01 = 0.51 \text{ M}$

This will alter the equilibrium problem:

Start:

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.49 \text{ M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.51 \text{ M}$$

$$[\text{H}^+] = 0$$

Equilibrium:

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.49 - A \text{ M}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.51 + A \text{ M}$$

$$[\text{H}^+] = A \text{ M}$$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(A)(0.51 + A)}{(0.49 - A)}$$

$$\text{so } A = 1.7 \times 10^{-5}$$

$$\text{and pH} = 4.76$$

The net change was 0.02 pH units

If 0.01 mol of NaOH had been added to a solution which did not contain the buffer, the pH would have gone to 12.0 (from 7.00); a change of 5.0 pH units!

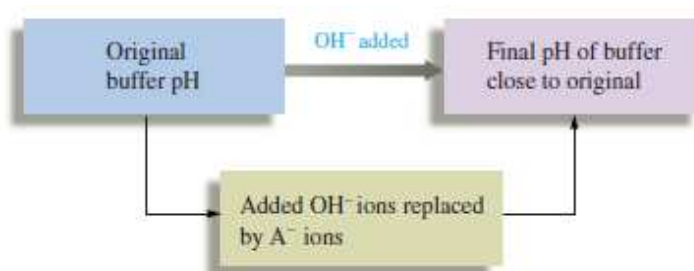
Buffering: How Does it Work

The easiest way to view the action of the resistance of the buffer to added OH^- is to recognize that it is being *replaced* by A^- . An added amount of H^+ in the form of strong acid would react with A^- producing the weak acid. This may be understood by considering the expression for the equilibrium constant:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

which, when rearranged, gives:

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$



The pH is determined by the ratio of [HA] to [A⁻]. By making sure that these concentrations are large compared to the amount of acid or base which might be added to the solution, the pH will be prevented from changing very much.

Taking logs of both sides of the above equation and changing the signs gives:

$$-\log([\text{H}^+]) = -\log(K_a) - \log([\text{HA}]/[\text{A}^-])$$

$$\text{pH} = \text{p}K_a - \log([\text{HA}]/[\text{A}^-]) = \text{p}K_a + \log([\text{base}]/[\text{acid}])$$

This is the *Henderson - Hasselbalch Equation*. It is valid to use the concentrations you calculate from the solution ingredients without worrying about the amount of HA that dissociates provided that this quantity is small - the usual situation:

Example: (15.4)

Calculate the pH of a solution of 0.75 M lactic acid (HC₃H₅O₃, K_a = 1.4x10⁻⁴) and 0.25 M sodium lactate. The pH will be controlled by the lactic acid/lactate equilibrium since H₂O is a much weaker acid.

Answer:

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$$

$$\text{pH} = 3.85 + \log(0.25/0.75) = 3.38$$

Buffers can also be made from weak bases and their conjugate acid:

Example: (15.5)

What is the pH of a solution containing 0.25 M NH₃ (K_b = 1.8x10⁻⁵) and 0.40 M NH₄Cl?

Answer:

Either:

- a. Use equation:



Go through the usual calculation to get the concentration of OH^- (1.1×10^{-5}), hence the pOH (4.95) and hence the pH (9.05).

Or:

- b. Use the equation:



Remember that:

$$K_a = K_w/K_b$$

Calculate K_a (5.6×10^{-10}), and then use the Henderson-Hasselbalch equation

$$\text{pH} = 9.25 + \log(0.25/0.40) = 9.05$$

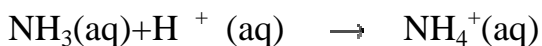
(Exercise 15.6)

Now add 0.10 mol of gaseous HCl to 1 L of the above ammonia/ammonium buffer solution. What is the new pH? Answer:

List the major species *before equilibration*:



Realize the ammonia will react with the H^+ which came from the HCl, and assume a quantitative reaction:



Start:

$$[\text{NH}_3] = 0.25 \text{ M}$$

$$[\text{NH}_4^+] = 0.40 \text{ M}$$

$$[\text{H}^+] = 0.10$$

At equilibrium:

$$[\text{NH}_3] = 0.25 - 0.10 = 0.15 \text{ M}$$

$$[\text{NH}_4^+] = 0.40 + 0.10 = 0.50 \text{ M}$$

$$[\text{H}^+] = 0$$

Finally use the Henderson - Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log(0.15)/(0.50) = 8.73$$

This is just a little down from 9.05. (Note that 0.1 mol of the acid was buffered as apposed to 0.01 M of the base in the sodium acetate example so the change was bigger.

3. Buffer Capacity

There are two scenarios presented in the text: The first (Exercise 15.7) compares two buffer solutions of different concentrations where the ratio of weak acid to its salt is near 1. The comparison asks the question "what is the effect of adding HCl to each of these?" The usual calculations are performed. The results are tabulated below:

Comparison of Buffer Capacities - Balanced Concentrations				
Solution	$[\text{C}_2\text{H}_3\text{O}_2^-]$ (M)	$[\text{HC}_2\text{H}_3\text{O}_2]$ (M)	Starting pH	pH with 0.01 M HCl
A	5.00	5.00	4.74	4.74
B	0.050	0.050	4.74	4.56

([Table](#))

The second scenario is adapted from the text where the weak acid to salt ratio is varied:

Comparison of Buffer Capacities - Unbalanced Concentrations					
Solution	[C₂H₃O₂⁻] (M)	[HC₂H₃O₂] (M)	Starting pH	pH with 0.01 M HCl	ΔpH
A	0.020	1.00	3.04	2.73	-0.31
B	1.00	1.00	4.74	4.73	0.01
C	1.00	0.020	6.43	6.44	-0.11

(Table)

The ideal buffer contains a roughly equal concentration of the weak acid or base and its salt, and a sufficient concentration of both to maximize the stabilization of the pH. This means choosing a buffer naturally close to the desired value. In the example (Exercise 15.8) the target pH is 4.30 and suggested buffers are listed below:

Pick a Buffer to Control the pH near 4.3		
Acid	K_a	pK_a
Chloroacetic Acid	1.35x10 ⁻³	2.87
Benzoic Acid	6.4x10 ⁻⁵	4.19
Propanoic Acid	1.3x10 ⁻⁵	4.89
Hypochlorous Acid	3.5x10 ⁻⁸	7.46

(Table)

4. Titration and pH curves

For convenience in experiments, calculations and graphs, the volumes are represented in mL of solution and molar quantities in millimoles (mmol). The key formulas remain unchanged, thus:

$$\# \text{ of moles (mmol)} = \text{volume (mL)} \times \text{molarity (M)}$$

for dilutions:

$$M_1 \text{ (M)} \times V_1 \text{ (mL)} = M_2 \text{ (M)} \times V_2 \text{ (mL)}$$

Strong Acid - Strong Base Titrations

Figure 15.1 shows a titration curve for the reaction of an aliquot of 50.0 mL of 0.200 M nitric acid (*analyte*) with 0.100 M sodium hydroxide (*titrant*). The points calculated appear below:

Titration of a Strong Acid (50 ml of 0.200 M HNO ₃) with a Strong Base (0.100 M NaOH)							
NaOH added	0	10.0	20.0	50.0	100.0	150.0	200.0
pH	0.699	0.820	0.942	1.30	7.00	12.40	12.60

(Table)

Notice on the graph that:

- The initial pH is very acid.
- The equivalence point is at pH = 7.00.
- The curve around the equivalence point is almost vertical.
- The vertical section is quite extended.
- The ending pH is very basic.

Titration of Weak Acids with Strong Bases

Figure 15.3 shows this titration:

Titration of a Weak Acid (50.0 mL of 0.100 Acetic) with a Strong Base (0.100 M NaOH)							
NaOH added	0	10.0	25.0	40.0	50.0	60.0	75.0
pH	2.87	4.14	4.74	5.35	8.72	11.96	12.30

(Table)

Notice on the graph that:

- The initial pH (2.87) is characteristic of a weak acid.
- From about 15 to 35 mL added the curve is very flat (buffer region), and flattest half way across to the equivalence point.
- The equivalence point is at 50 mL of NaOH added and the pH is 8.72 ie *basic* due to the conjugate basicity of the base acetate.
- At the equivalence point, the curve is not steep as long as for the strong acid/strong base case, but the equivalence point is still at the point of the 1:1 stoichiometric ratio of titrant to analyte.

Figure 15.4 shows curves for a series of hypothetical acids of differing pK_a values. Notice that:

- The steep section gets shorter and shorter in terms of the pH range - this will be important for indicator choice.
- The steep portion is always at the same volume of NaOH - the equivalence point

Calculation of pK_a

(The following calculation is related to the last Lab experiment.) Example: (Exercise 15.10)

2.00 mmol of a weak monoprotic acid are dissolved in 100 mL of water and the solution titrated with 0.050 M NaOH solution. After 20.0 mL of the NaOH have been added the pH is 6.00. What is the pK_a of the acid?

Answer:

Deal first with the stoichiometric problem:



Before titration:

$$\text{HA} = 2.00 \text{ mmol}$$

$$\text{OH}^- = 20.0 \text{ mL} \times 0.0500 \text{ M} = 1.00 \text{ mmol}$$

$$\text{A}^- = 0$$

After titration:

$$\text{HA} = 2.00 - 1.00 \text{ mmol}$$

$$\text{OH}^- = 1.00 - 1.00 = 0$$

$$\text{A}^- = 1.00$$

Now handle the equilibrium problem:

Major species: HA, A^- , Na^+ , H_2O



Start *concentrations*:

$$[\text{HA}] = 1.00 \text{ mmol} / (100.0 + 20.0) \text{ mL} = 8.33 \times 10^{-3} \text{ M}$$

$$[\text{A}^-] = 1.00 \text{ mmol} / (100.0 + 20.0) \text{ mL} = 8.33 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = 0$$

Equilibrium concentrations:

$$[\text{HA}] = 1.00 \text{ mmol} / (100.0 + 20.0) \text{ mL} = 8.33 \times 10^{-3} - A \text{ M}$$

$$[\text{A}^-] = 1.00 \text{ mmol} / (100.0 + 20.0) \text{ mL} = 8.33 \times 10^{-3} + A \text{ M}$$

$$[\text{H}^+] = A$$

Now we know $[\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-6.00) = 1.0 \times 10^{-6} \text{ M}$.

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] = 1.0 \times 10^{-6}$$

Actually we should have noticed that the NaOH added contained 1.00 mmol of OH⁻ whereas the original solution contained 2.00 mmol of acid therefore we were at the halfway point of the titration where [HA] = [A⁻]. At this point the pH = K_a!

Titration of Weak Bases with Strong Acids

This is similar to the weak acid/strong base case. Sample data are given below for the titration of 100 mL of 0.050 M NH₃ solution with 0.10 M HCl:

Titration of a Weak Base (100 mL of 0.050 M NH ₃) with a Strong Acid (0.10 M HCl)					
NaOH added	0	10.0	25.0	50.0	60.0
pH	10.6	9.85	9.25	5.36	2.21

(Table)

These data are plotted in **Figure 15.5**. Notice:

- The buffer region around pH = 9.25 at 25 mL acid added.
- The equivalence point at 50.0 mL.
- The final pH is determined by the excess H⁺.

2. Acid-Base Indicators

While a pH meter can always be used to plot the course of a titration, it is possible to determine the equivalence point by picking a suitable indicator whose colour changes at the pH that would occur during the steep part of the curve.

Indicators are weak acids (or bases) whose conjugate bases (or acids) are different colours. Such an indicator is phenolphthalein (**Figure 15.6**) which has a pK_a of 8.00. Remember that this is the pH at which half the phenolphthalein will be in the protonated (acid) form and the

rest present as the conjugate base. The acid form of phenolphthalein is colorless and the basic form is pink.

Actually, our eyes can detect a colour change when about 10% of indicator changes form: the book example is bromothymol blue which is yellow in its acid form and blue when basic. In titrating an acid, the first tinge of greenishness can be seen when 10% of the basic form is present. Using the Henderson-Hasselbalch equation, the book shows that this corresponds to a point 1 pH unit to the acid side of its pK_a . Similarly, going in the opposite direction, the first tinge of yellow in the blue basic form would be seen 1 pH unit to the basic side of the pK_a value. Since $pK_a = 7$ for bromthymol blue, its colour change will occur from $pH = 6$ to $pH = 8$. (Usually, the colour change is more easily seen going in one direction, for example it is much easier to detect the first tinge of pink with phenolphthalein going from acid to base than trying to detect the beginning of the disappearance of the pink colour going the other way. Similarly the yellow to blue direction is better for bromthymol blue.

For strong acid/ strong base titrations, there is a long vertical part to the curve around the equivalence point and many indicators will change in this range (**Figure 15.8**). For a titration of 100.0 mL of 0.1 M HCl with 0.1 M NaOH, the pH changes from 5.3 to 8.7 within 0.01 mL of the equivalence point. One drop is about 0.04 mL.

For weak acid or weak base titrations, the indicator must be much more carefully chosen. **Figures 15.9** and **15.10** illustrate this.

Titration Simulator



Click on the "Start" button to bring up the applet window.

- Select the acid, base, their concentrations, which of them is in the burette, and choose an indicator.
Important. After altering the concentrations, press return or the altered values will not be registered.
- Click on the burette stopcock to start or stop the titration.
- Use the scroll bar to adjust the dropping rate
- Click in the graph area to clear it.

- Click on the burette column to set the starting level.

Note: The method used to calculate the pH and generate the curves is the same as that in the text, though the full the quadratic solution is always used, that is, the "usual approximation" is not applied. However, the contribution to $[H^+]$ from the auto-ionization of water is ignored (as it is in the text). For very dilute solutions and/or very weak acids or bases, this leads to a discontinuity in the curve near the equivalence point which would not appear in a real experimental plot.

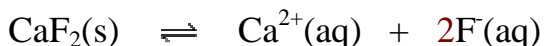
Solubility Equilibria:

6. Solubility Equilibria and the Solubility Product

Preliminary examples of the importance of treating solubility phenomena are:

- $CaCO_3$ "fur" on pipes.
- $BaSO_4$ as an X-ray opaque compound.
- Apatite $Ca_5(PO_4)_3OH$ vs fluorapatite $Ca_5(PO_4)_3F$ in preventing tooth decay.

Solubility can be treated as another equilibrium phenomenon e.g.:



It must be understood that equilibrium is a dynamic situation with solid going into solution and dissolved material redepositing. Over time, crystals in contact with a saturated solution may change their shape although the mass of the solid will not change.

The appropriate equilibrium constant is called the solubility product. For CaF_2 it would be:

$$K_{sp} = [Ca^{2+}][F^-]^2$$

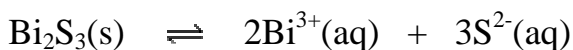
(Table 15.4 is a fairly extensive table of solubility products for rather insoluble ionic solids.) Note that the solubility constant is constant but the actual solubility will depend on the presence of common ions.

The calculation of K_{sp} from a known solubility is trivial:

Exercise 15.13

Calculate the K_{sp} value for Bi_2S_3 which has a solubility of 1.0×10^{-15} M in pure water.

Answer: The equation is:



$$K_{\text{sp}} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3$$

The concentrations can be obtained directly from the chemical equation and plugged into the formula for K_{sp} .

$$[\text{Bi}^{3+}] = 2 \times 1.0 \times 10^{-15} \text{ M}$$

$$[\text{S}^{2-}] = 3 \times 1.0 \times 10^{-15} \text{ M}$$

$$K_{\text{sp}} = (2.0 \times 10^{-15})^2 (3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

The calculation of solubility from the solubility constant can be more tricky:

Exercise 15.14

The K_{sp} value for copper(II) iodate at 25 °C is 1.4×10^{-7} . Calculate its solubility in pure water.

Answer: The equations are:



$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_3^{-}]^2$$

Let the equilibrium concentrations be:

$$[\text{Cu}^{2+}] = A$$

$$[\text{IO}_3^{-}] = 2A$$

$$1.4 \times 10^{-7} = (A)(2A)^2 = 4A^3$$

$$A = 3.3 \times 10^{-3} \text{ M}$$

Relative Solubilities

This section is merely a warning that K_{sp} values must be used with care to compare solubilities of similar species. Examples are:

Solubility Data for Selected Compounds

Salt	K_{sp}	Solubility Equation	Solubility (mol/L)
CaCO_3	8.7×10^{-9}	$(K_{sp})^{1/2}$	9.3×10^{-5}
SrCO_3	7×10^{-10}	$(K_{sp})^{1/2}$	3×10^{-5}
BaCO_3	1.6×10^{-9} <small><SUP> TD></small>	$(K_{sp})^{1/2}$	4.0×10^{-5}
CuS	8.4×10^{-45}	$(K_{sp})^{1/2}$	9.2×10^{-25}
Ag_2S	1.6×10^{-49}	$(K_{sp}/4)^{1/3}$	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	$(K_{sp}/108)^{1/5}$	1.0×10^{-15}

(Table)

Common Ion Effect

Example:

Consider the solubility of silver chromate ($K_{sp} = 9.0 \times 10^{-12}$) in a 0.100 M solution of silver nitrate.

Answer:



Starting concentrations

$$[\text{Ag}^+] = 0.100 \text{ M}$$

$$[\text{CrO}_4^{2-}] = 0$$

Equilibrium concentrations

$$[\text{Ag}^+] = 0.100 + 2A \text{ M}$$

$$[\text{CrO}_4^{2-}] = A$$

Therefore:

$$K_{sp} = 9.0 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (0.100 + 2A)^2(A)$$

This will make a cubic equation but we can make the usual approximation since A will be very small compared to 0.100:

$$9.0 \times 10^{-12} = (0.100)^2(A) \quad \text{so } A = 9.0 \times 10^{-10} \text{ M}$$

Compare this with the solubility of Ag_2CrO_4 in pure water - 1.3×10^{-4} M.

pH and Solubility

This section is about certain cases where the concentration of one of the ions of the rather insoluble compound is modified by the pH. An obvious example is where the anion is hydroxide: the text cites $\text{Mg}(\text{OH})_2$. The addition of acid to a solution in equilibrium with solid $\text{Mg}(\text{OH})_2$ will reduce the OH^- concentration and therefore Mg^{2+} can be present at a much higher concentration.

Another example is Ag_3PO_4 where the presence of acid will convert PO_4^{3-} to HPO_4^{2-} . Silver ions can enter the solution since the silver hydrogen phosphate is more soluble.

Generally, if the anion of an insoluble compound has appreciable basic properties, the compound will tend to be more soluble in acidic solutions.

7. Precipitation and Qualitative Analysis

One of the main methods in classical qualitative analysis (the detection of ions present rather than their quantitative estimation) relies on creating the conditions for precipitation. The equivalent of the reaction quotient (Q) for precipitations is called the *ion product*, also given the symbol Q. If two solutions are mixed resulting in a potential precipitation, if $Q > K_{sp}$, a precipitate will form.

Example:

Mix 100.0 mL of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ with 200.0 mL of 0.100 M NaI. Given that K_{sp} for $\text{PbI}_2 = 1.4 \times 10^{-8}$ what will be the final concentrations of ions in the solution?

The first step is to determine the concentrations assuming no precipitation:

Assume the new volume is 300 mL and use $M_1 \cdot V_1 = M_2 \cdot V_2$

$$[\text{Pb}^{2+}] = (100.0 \times 0.0500) / 300.0 = 1.67 \times 10^{-2} \text{ M}$$

$$([\text{NO}_3^-] = 2 \times [\text{Pb}^{2+}])$$

$$[\text{I}^-] = (200.0 \times 0.100) / 300.0 = 6.67 \times 10^{-2} \text{ M}$$

$$([\text{Na}^+] = [\text{I}^-])$$

Only the PbI_2 will perhaps precipitate - other combinations are clearly soluble at the new concentrations. Calculation of Q will confirm this:

$$Q = [\text{Pb}^{2+}][\text{I}^-]^2 = (1.67 \times 10^{-2})(6.67 \times 10^{-2})^2 = 7.43 \times 10^{-5} (> 1.4 \times 10^{-8})$$

The next step is to pretend that all the PbI_2 that can be formed precipitates:

Start:

$$\text{Amount of Pb}^{2+} = 100.0 \times 0.0500 = 5.00 \text{ mmol}$$

$$\text{Amount of I}^- = 200.0 \times 0.100 = 20.0 \text{ mmol}$$

(ie an excess because only 10.0 mmol combine with the 5.00 mmol of Pb^{2+})

After formation of PbI_2 and assuming it all precipitates for the moment:

10.0 mmol of I^- remain in 300 mL of the solution

ie it is $10.0 / 300.0 = 3.33 \times 10^{-2} \text{ M}$ in I^- .

The next step exactly parallels the common ion problem. Start:

$$[\text{Pb}^{2+}] = 0$$

$$[\text{I}^-] = 3.33 \times 10^{-2} \text{ M}$$

At equilibrium:

$$[\text{Pb}^{2+}] = A$$

$$[\text{I}^-] = 3.33 \times 10^{-2} + 2A \text{ M}$$

Therefore:

$$K_{\text{sp}} = 1.4 \times 10^{-8} = [\text{Pb}^{2+}][\text{I}^-]^2 = (A)(3.33 \times 10^{-2} + 2A)^2$$

$$\sim (A)(3.33 \times 10^{-2})^2$$

$$[\text{Pb}^{2+}] = A = 1.3 \times 10^{-5} \text{ M and } [\text{I}^-] = 3.33 \times 10^{-2} \text{ M}$$

Selective Precipitation

By carefully choosing the conditions we can arrange to precipitate only selected ions in a solution containing more than one.

Example:

A solution contains $1.0 \times 10^{-4} \text{ M Cu}^+$ and $2.0 \times 10^{-3} \text{ M Pb}^{2+}$. If a source of I^- is gradually added to the solution, which iodide will precipitate first? ($K_{\text{sp}}(\text{CuI}) = 5.3 \times 10^{-12}$, $K_{\text{sp}}(\text{PbI}_2) = 1.4 \times 10^{-8}$.)

Answer:

Calculate the greatest concentration of I^- that can be present before precipitation of each iodide and compare:

For CuI :

$$K_{\text{sp}} = [\text{Cu}^+][\text{I}^-]_{\text{max}} = (1.0 \times 10^{-4})[\text{I}^-]_{\text{max}} = 5.3 \times 10^{-8}$$
$$\text{so } [\text{I}^-]_{\text{max}} = 5.3 \times 10^{-12} \text{ M}$$

For PbI_2

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]_{\text{max}}^2 = (2 \times 10^{-3})[\text{I}^-]_{\text{max}}^2 = 1.4 \times 10^{-8}$$
$$\text{so } [\text{I}^-]_{\text{max}} = 2.6 \times 10^{-8} \text{ M}$$

Clearly the copper compound precipitates first.

Example:

In one of the lab experiments, 5 mL of a saturated solution of sodium chloride (approx 5 M) was treated with 10 drops (about 0.4 ml) of 1 M hydrochloric acid, and in another test with 10 drops of 12 M (concentrated) hydrochloric acid. Rationalize the fact that a precipitate was not formed with the 1 M acid but did form with the 12 M acid. Answer:

The saturated sodium chloride solution has $[\text{Na}^+] = 5 \text{ M}$ and $[\text{Cl}^-] = 5 \text{ M}$ so $K_{\text{sp}} = [\text{Na}^+][\text{Cl}^-] = 5 \times 5 = 25$

After the addition of the 10 drops of acid, the volume of the solution is $5.0 + 0.4 = 5.4 \text{ mL}$

The new $[\text{Na}^+] = 5 \times 5.0/5.4 = 4.6 \text{ M}$

With the 1 M HCl, the final $[\text{Cl}^-] = (5 \times 5.0/5.4) + (1 \times 0.4/5.4) = 4.67 \text{ M}$

In this case $Q = 4.6 \times 4.67 = 21.5$ which is less than 25, so no precipitate should form.

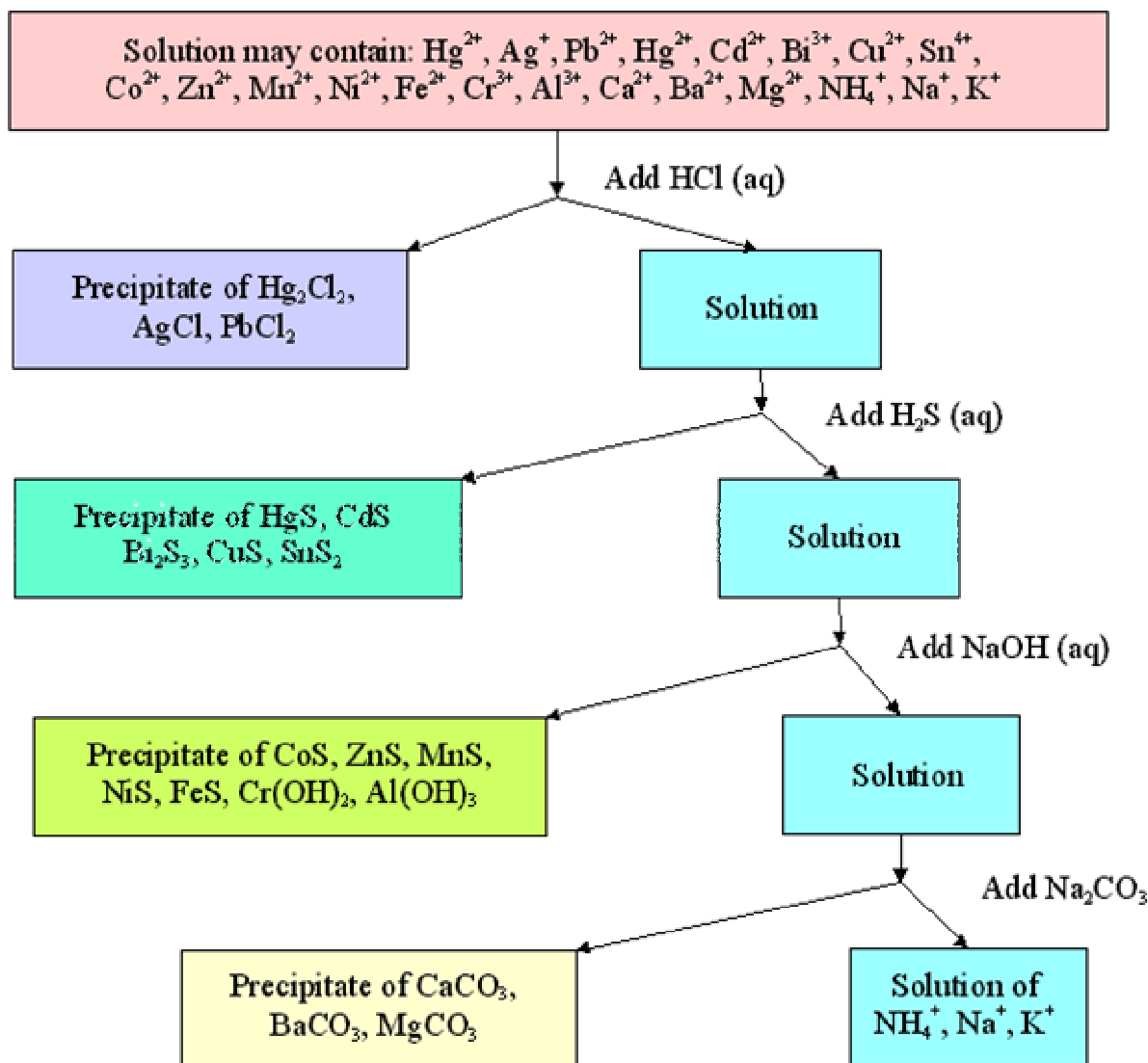
With the 12 M HCl, the final $[\text{Cl}^-] = (5 \times 5.0/5.4) + (12 \times 0.4/5.4) = 5.49$

In this case $Q = 4.6 \times 5.9 = 25.3$ which is greater than 25, so a precipitate is expected unless the solution supersaturates in the absence of any suitable nucleation sites.

Qualitative Analysis

The foregoing concept has been extended to allow the separation of very many metal ions.

The Classic Separation of Common Cations



Complex Ion Equilibria

8. Equilibria Involving Complex Ions

Some common *ligands*:

H_2O , NH_3 , Cl^- , CN^-

Some less common ligands used in analytical chemistry:

EDTA, ethylene diamine, 8-hydroxyquinoline, dimethylglyoxime

Examples of *coordination numbers* and complex ions:

$\text{Co}(\text{H}_2\text{O})_6^{2+}$ 6-coordinate, pink

$\text{Ni}(\text{NH}_3)_6^{2+}$ 6-coordinate, green

CoCl_4^{2-} 4-coordinate, blue

$\text{Ag}(\text{NH}_3)_2^+$ 2-coordinate, colourless

Example of stepwise *formation* or *stability constants*:



Provided the ligand is present in excess, the calculations are not complicated.

Example:

What are the concentrations of the silver containing ions in a mixture of 100.0 mL of 2.0 M NH_3 and 100.0 mL of 1.0×10^{-3} M AgNO_3 ?

Answer:

the major solution species are: Ag^+ , NO_3^- , NH_3 and H_2O but only the NH_3/Ag^+ system is of interest.

Start:

$$[\text{Ag}^+]_0 = (100.0)(1.0 \times 10^{-3}) / (200.0) = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{NH}_3]_0 = (100.0)(2.0) / (200.0) = 1.00 \text{ M}$$

Assume essentially complete reaction to give 5.0×10^{-4} M $\text{Ag}(\text{NH}_3)_2^+$ because the equilibrium constants are large, and then consider these equilibria:

Let $[\text{Ag}(\text{NH}_3)^+] = A$ and assume negligible NH_3 has been consumed:

$$K_2 = 8.2 \times 10^3 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} =$$

$$(5.0 \times 10^{-4} - A)/(A)(1.0 + A) \sim (5.0 \times 10^{-4})/(A)(1.0)$$

$$A = [\text{Ag}(\text{NH}_3)^+] = 6.1 \times 10^{-8} \text{ M}$$

Now Let $[\text{Ag}^+] = A$ and still assume negligible NH_3 has been consumed:

$$K_1 = 2.1 \times 10^3 = [\text{Ag}(\text{NH}_3)^+]/[\text{Ag}^+][\text{NH}_3] =$$

$$(6.1 \times 10^{-8} - A)/(A)(1.0 + A) \sim (6.1 \times 10^{-8})/(A)(1.0)$$

$$A = [\text{Ag}^+] = 2.9 \times 10^{-11} \text{ M}$$

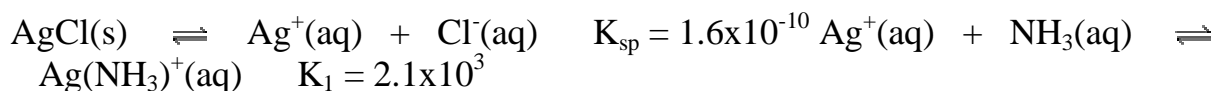
$$\text{i.e. } [\text{Ag}(\text{NH}_3)_2^+] \gg [\text{Ag}(\text{NH}_3)^+] \gg [\text{Ag}^+]$$

Complex Ions and Solubility

Recall the classical ion separation table. The first set of compounds precipitated were:

AgCl , PbCl and Hg_2Cl_2

The Ag^+ can be redissolved by adding NH_3 and complexing it in the following sequence of steps:



The net reaction is:



$$K = [\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]/[\text{NH}_3]^2 = K_{\text{sp}} \cdot K_1 \cdot K_2 = 2.8 \times 10^{-3}$$

Example:

Calculate the solubility of AgCl in 10 M NH_3 solution.

Answer:



Start:

$$[\text{NH}_3] = 10 \text{ M}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = 0$$

$$[\text{Cl}^-] = 0$$

At equilibrium:

$$[\text{NH}_3] = 10 - 2A \text{ M}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = A$$

$$[\text{Cl}^-] = A$$

$$(2.8 \times 10^{-3})^{1/2} = ((A)(A)/(10 - 2A)^2)^{1/2} = ((A)(A)/(10)^2)^{1/2}$$

$$A = 0.48 \text{ mol/L}$$

Note that the solubility of AgCl in pure water = $(K_{sp})^{1/2} = 1.3 \times 10^{-5} \text{ mol/L}$

This is one factor that leads to the separation scheme for the above three species:

Classical Separation of the Insoluble Chlorides

