The Common-Ion Effect

- weak acid or weak base will partially ionize in aqueous solution.

- Ionic compounds (i.e. salts) dissociate completely in aqueous solution

    - Some salts may contain ions derived from acids or bases
    - Ions derived from strong acids or bases will not alter the pH
    - Ions derived from weak acids or bases will have a tendency to affect pH, either donate or accept a proton

What happens if a salt is added to a solution of a weak acid, and that salt contains a conjugate base to the weak acid?

Example: Acetic acid ($HC_2H_3O_2$)

The ionization of acetic acid, a weak acid, is as follows:

$$HC_2H_3O_2(aq) \Leftrightarrow C_2H_3O_2^-(aq) + H^+(aq)$$

add some Sodium Acetate salt.

- Sodium acetate will dissociate completely in solution:

$$NaC_2H_3O_2(aq) \rightarrow Na^+(aq) + C_2H_3O_2^-(aq)$$

- We have increased the acetate conjugate base concentration (*without increasing the concentration of H+*)
- Le Chatelier's - equilibrium will *shift to the left*

$$HC_2H_3O_2(aq) \leftarrow C_2H_3O_2^-(aq) + H^+(aq)$$

- will also result in a decrease in the H+ concentration – raise pH
- *less acid will dissociate*

The "Common Ion Effect": *The dissociation of a weak electrolyte is decreased by adding to the solution a strong electrolyte (i.e. a salt) that has an ion in common with the weak electrolyte*

Example

Acetic acid (CH_3COOH) is a weak acid with the following ionization reaction:

$$CH_3COOH + H_2O \Leftrightarrow H_3O^+ + CH_3COO^- \quad Ka = 1.8 \times 10_{-5}$$

What is the pH of a solution that is 0.5M in acetic acid and 2.5M in sodium acetate, CH_3COONa?

$$1.8 \times 10^{-5} = [CH_3COO^-][H_3O^+]/[CH_3COOH]$$

X M = amount of acetic acid that dissociates then X M of H_3O+ and CH_3COO- ions are formed

$1.8 \times 10^{-5} = (X + 2.5)(X)/(0.5 - X)$

Can we use the shortcut to the quadratic?

0.5M acetic acid / $1.8 \times 10^{-5} = 27,777$ (which is greater than 100)

$1.8 \times 10^{-5} = (X + 2.5)(X)/(0.5 - X) \approx (2.5)(X)/(0.5)$

$9.0 \times 10^{-6} = 2.5X$

$X = 3.60 \times 10^{-6} = [H+]$

pH = -log[H+] = $-\log(3.60 \times 10^{-6}) = 5.44$

Example 2

What is the pH of an aqueous solution that contains 0.15M NH_3 and 0.05M $(NH_4)_2SO_4$? The Kb for NH_3 is 1.8×10^{-5}.

- The 0.05M of $(NH_4)_2SO_4$salt will dissociate completely to produce 0.1M of NH_4+

$$(NH_4)_2SO_4\ (aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}\ (aq)$$

- Ammonia will ionize to produce NH_4+ and OH- according to the value for Kb

$$NH_3(aq) + H_2O(l) \Leftrightarrow NH_4+(aq) + OH-(aq)$$

and at equilibrium:

$$K_b = 1.8 * 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Set X = amount of NH3 that will ionize as the reaction goes to equilibrium

- The added salt is not directly altering the concentration of either NH_3 or OH-
- Therefore if X M of NH_3 ionize, then X M of OH- are produced at equilibrium
- The concentration of NH_4+ at equilibrium is equal to the amount of NH_3 that ionizes, plus the added amount of NH_4+ from the salt (X + 0.1M)

• The concentration of NH_3 at equilibrium is equal to the starting concentration minus the amount that ionized (0.15M - X)

We can now set up the equilibrium expression:

$Kb = 1.8 \times 10^{-5} = (X + 0.1)(X) / (0.15 - X)$

Therefore, at equilibrium:
- $[OH-] = 2.7 \times 10^{-5}$ M
- $[NH_4+] = (X + 0.1M) \sim 0.100M$
- $[NH_3] = (0.15 - X) \sim 0.150M$
- pOH = -log[OH-] = 4.57

- pH = (14 - pOH) = 9.43

If no salt:

Therefore at equilibrium:
- $[NH_3]$ = 0.15 - 1.63 x 10^{-3} = 0.148M
- [OH-] = 1.63 x 10^{-3}
- $[NH_4+]$ = 1.63 x 10^{-3}
- pOH = -log[OH-] = 2.79
- pH = 14 - pOH = 11.2

Buffered Solutions

Solutions that resist a change in pH upon addition of small amounts of acid or base are called "Buffered" solutions (or just "Buffers")

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

This simple analysis provides a clue as to the various entities that can influence the [H+], and therefore, the pH:
- The value of the acid dissociation constant Ka
  - The ratio of the concentration of acid to conjugate base

Again, if the concentrations of [HA] and [A-] are large to begin with, and if the added concentration of H+ is small, the change in pH upon addition of the H+ will be small (the pH of the solution will be buffered)

buffers work best when the ratio of [HA]/[A-] is 1.0. (In other words, if the concentration of either HA or A- is small, the solution can't buffer very well)
- From the above equation, if [HA]/[A-] = 1.0, then [H+] = Ka

if you want to buffer a solution at pH = 8.5 choose a weak acid/base conjugate pair whose pKa = 8.5. (log Ka = -8.5, Ka = 3.16 x 10^{-9}; hypobromous acid is sort of close, pKa = 2.5 x 10^{-9})

*The **greater the concentrations** of both [HA] and [A-] (i.e. the acid/conjugate base-pair) the greater the buffering capacity*

Henderson-Hasselbalch

$$-\log\left[H^+\right] = -\log\left(K_a \frac{[HA]}{[A^-]}\right)$$

$$pH = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

Example: What is the pH of a buffer that is 0.15M in acetic acid (CH_3COOH) and 0.05M in sodium acetate ($NaCH_3COO$)? The Ka for acetic acid is 1.8 x 10^{-5}.

We assume that a very small percentage of the acid will ionize as the process goes to equilibrium. lead to the conclusion that we can use the starting concentrations of acid and conjugate base as a good estimate of the equilibrium concentrations

pH = -log(1.8 x 10^{-5}) + log(0.05/0.15)

pH = 4.74 - 0.477

pH = 4.26

In the above problem, what would the pH be if 0.01M of NaOH is added to the buffer?

the NaOH is a strong base and will dissociate completely.
The OH- ion will make the solution more basic.
From the balanced equation, we see that removal of H+ will shift the equilibrium to the right:

CH3COOH(*aq*) ⇔ CH3COO-(*aq*) + H+(*aq*)

The 0.01M of OH- ions can react stoichiometrically with 0.01M of H+, and 0.01M of H+ is produced from the ionization of 0.01M of acetic acid. ***Therefore, addition of 0.01M of NaOH will reduce the concentration of acetic acid by 0.01M, and increase the concentration of conjugate base (acetate ion) by 0.01M***.

pH = -log(1.8 x 10^{-5}) + log((0.05+0.01)/(0.15-0.01))

pH = 4.74 + log(0.06/0.14)

pH = 4.74 - 0.368

pH = 4.37

Acid-Base Titrations

the ***equivalence point*** is the point at which a stoichiometrically equivalent amount of base has been added to the acid

- A graph or plot of the pH as a function of added titrant (e.g. base solution) is called a ***titration curve***

Strong Acid - Strong Base Titrations

What happens when a stoichiometrically equivalent amount of strong base is added to a solution of a strong acid?

- All of the H+ ions present in the acid react with an equivalent amount of OH- ions from the base; and there are no net H+ or OH- ions left over (i.e. [H+] = [OH-]). The reaction of the H+ and OH- ions produces H2O(*l*)
- Also, [Na+] = [Cl-], and we essentially have a solution of H2O and NaCl(*aq*)
- Since the NaCl produced has no effect upon pH, *when an equivalent amount of NaOH is added to a solution of HCl the solution has a neutral pH (i.e. pH = 7.0)*

What happens if a less-than-stoichiometrically equivalent amount of strong base is added to the strong acid solution?

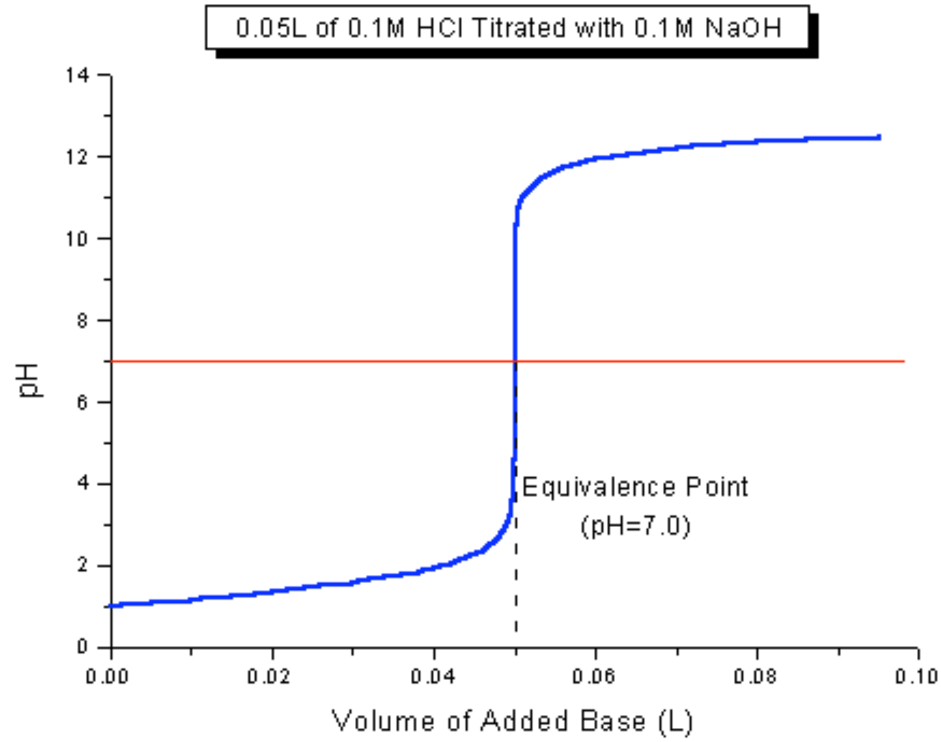
- For the NaOH that is added, all of it will ionize, and all of the OH- ions added will react with acid (to produce Na+ and H2O(*l*))
- Since the NaOH that was added is less than the concentration of HCl acid, there will be remaining H+ ions and Cl- ions

The solution will contain H+, Cl- and Na+ ions (essentially no OH- ions)

- The [Cl-] will be greater than [Na+] in this case, but who cares? We have already determined that they don't affect the pH anyway. Thus, the solution will be acidic if less-than-stoichiometrically equivalent amount of base is added
- The concentration of [H+] ion will be equal to the starting concentration minus the amount that is neutralized. The amount that is neutralized is equal to the concentration of added base. The pH of the solution will be determined by the amount of [H+] remaining after this neutralization

What happens if a greater-than-stoichiometrically equivalent amount of base is added to the acid solution?

- All H+ from the acid are neutralized (essentially no H+ from the acid remains)
- There will be Cl- ions, Na+ ions and OH- ions in solution. Thus, the solution will be basic.
- The [Na+] will be greater than [Cl-], but who cares? These ions don't affect pH. Thus, the pH will depend upon the concentration of the OH- ions in solution.
  - The concentration of OH- ions will be equal to the amount of basic solution added minus the amount that is neutralized. The amount neutralized is equal to the concentration of acid in the original sample.



The Addition of a Strong Base to a Weak Acid

Calculate the pH of a solution of a weak acid with Ka = 1.8 x 10-4 after 10ml of 0.1M NaOH has been titrated into a 50ml solution of 0.2M weak acid.

- First of all, how many total moles of weak acid do we have?

(.05L * 0.2moles/L) = 0.01moles

- How many moles of strong base were added?

(0.01L * 0.1moles/L) = 0.001moles

- Since 0.001moles of base were added, 0.001moles of acid were neutralized (leaving 0.009 moles of weak acid), and 0.001moles of conjugate base were produced
- The volume of the sample after addition of the base is now (0.05 + 0.01L) = 0.06L. Therefore, we have the following concentrations of weak acid and conjugate base:

0.009moles/0.06L = 0.15M HA (weak acid)

0.001moles/0.06L = 0.0167M A- (conjugate base)

- The balanced equation and equilibrium expression are:

HA(*aq*) ⇔ H+(*aq*) + A-(*aq*)

Ka = [H+]*[A-] / [HA]

Or

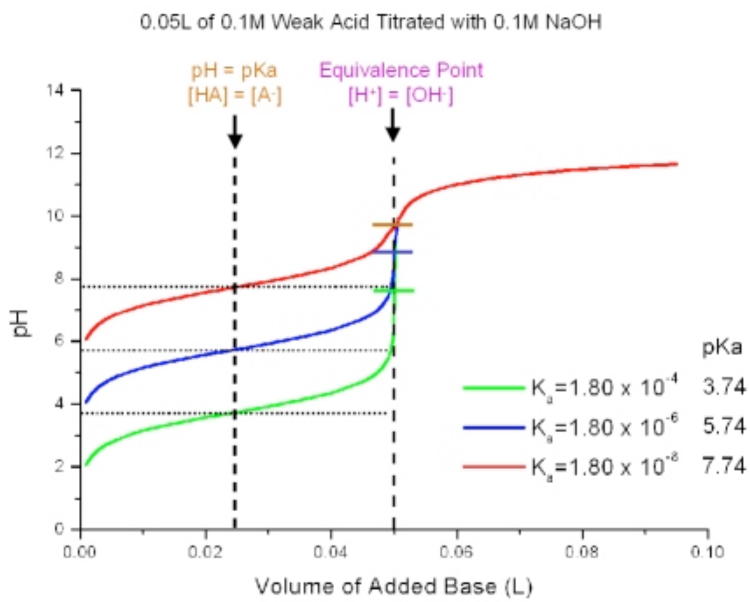
[H+] = Ka * [HA] / [A-]
(one form of the Henderson-Hasselbalch equation)

[H+] = 1.8 x 10-4 * 0.15 / 0.0167

[H+] = 1.62 x 10-3

pH = 2.79

Titration Curves of Weak Acids with a Strong Base



- At the equivalence point the solution contains only the salt
    - However, for a weak acid, the salt contains the conjugate base, which is able to recombine with a proton.

Thus, at the equivalence point of the titration of a weak acid with a strong base, the solution is slightly basic

- After the equivalence point, the solution contains salt and excess (i.e. non-neutralized) base (OH-). The pH of the solution after the equivalence point is determined mainly by the excess OH- ions provided by the strong base

Solubility Equilibria

- An ionic solid may dissolve in water, but, how much will dissolve?
- If enough ionic solid is added to a solvent, some will dissolve but some will be left as undissolved solid
    - Is there a way to predict how much of a particular ionic solid will dissolve in a solution?

The Solubility-Product Constant, Ksp

$BaSO_4(s) \Leftrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$

heterogeneous equilibrium- ignore solid

$$K = \frac{[Ba^{2+}(aq)][SO_4^{2-}(aq)]}{[BaSO_4(s)]}$$

$$K_{sp} = K[BaSO4(s)] = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$$

The smaller the value of Ksp, ***the lower the solubility*** *of the ions of an ionic solid*

Solubility and Ksp

Solubility
- *The amount of a substance that dissolves when producing a saturated solution*
- *Solubility can be expressed in g/L or as molar solubility (i.e. mol/L)*

Solubility product constant (Ksp)
- *Describes the concentration(s) of dissolved ions, or substance(s), at saturation equilibrium*

The solubility of a substance may change as the concentrations of various ions change (including H+), however, the value of Ksp is unique for a given solute at a specified temperature.

A solution of Copper(I)chloride (CuCl) is made such that a solid amount remains after equilibrium (i.e. after a couple of days some solid remains undissolved). The concentration of Cu+(aq) ion is determined to be 1.10×10^{-3} M. What is the value of the solubility product constant, Ksp?

CuCl → Cu+(aq) + Cl-(aq)

Ksp = [Cu+][Cl-]

From the stoichiometry of the balanced equation, at equilibrium [Cu+] = [Cl-]. Therefore, [Cu+] = [Cl-] = 1.10×10^{-3} M. Thus:

Ksp = $(1.10 \times 10^{-3}) * (1.10 \times 10^{-3})$

Ksp = 1.21×10^{-6}

What is the solubility of CuCl in g/L?

At equilbrium the molar concentration of Cu+(aq) will be 1.10×10^{-3} M, and the molar *concentration of Cl-(aq) ion will be 1.10×10^{-3} M*

*For Cu+(aq): 1.10×10^{-3} mol/L * (63.5g/mol) = 0.0699g/L*

*For Cl-(aq): 1.10×10^{-3} mol/L * (35.4g/mol) = 0.0389g/L*

Thus, a total of (0.0699 + 0.0389) = 0.109g/L of CuCl solid will dissolve (i.e. the solubility of CuCl is 0.109g/L)

Factors that Affect Solubility

There are three effects upon the solubility of a compound that we need to consider:

1 The presence of *common ions*

2 The *pH* of the solution (i.e. the effect of [H+] or [OH-] on the solubility)
3 The presence of *complexing agents*

1) Here is an example of how the solubility can change, but the solubility product constant is the same:

What is the solubility of CuCl in an aqueous solution of 0.01M NaCl?

CuCl → Cu+(aq) + Cl-(aq)

Ksp = [Cu+][Cl-] = 1.21×10^{-6}

XM = amount of CuCl that dissolves in the NaCl solution

Therefore at equilibrium we have XM of Cu+(aq) and (0.01 + XM) of Cl-(aq)

Ksp = [Cu+][Cl-] = 1.21×10^{-6} = (X)(0.01 + X)

X^2 + 0.01X - 1.21 x 10-6 = 0

This is a quadratic with a solution X = 1.20×10^{-4} M

This is the solubility of CuCl in the NaCl solution. At equilibrium we would therefore have 1.20×10^{-4} M of Cu+(aq) and (0.01 + 1.20×10^{-4}) = 1.01×10^{-2} M of Cl-(aq). Checking the value for Ksp with these concentrations:

Ksp = [Cu+][Cl-] = (1.20×10^{-4})(1.01×10^{-2}) = 1.21 x 10-6

Thus, the presence of the NaCl has changed the solubility of the CuCl, but the Ksp is an intrinsic constant.

2) **Solubility and pH**

$Mg(OH)_2(s) \Leftrightarrow Mg^{2+}(aq) + 2OH^-(aq)$

$Ksp = [Mg^{2+}] [OH-]^2 = 1.8 \times 10^{-11}$

$Ksp = [X] * [2X]^2 = 1.8 \times 10^{-11}$

$4X^3 = 1.8 \times 10^{-11}$

$X = 1.04 \times 10^{-4}$ M
- The [Mg2+] at equilibrium equals 1.04×10^{-4}
- The [OH-] at equilibrium equals 2.08×10^{-4}M
- The pOH therefore equals 3.68, and pH is therefore (14.0 - 3.68) = 10.3

If the same $Mg(OH)_2$ solution is made in a buffer at pH 9.0, what is the effect upon the solubility?
- At pH = 9.0, the pOH = (14 - 9.0) = 5.0
- Therefore, the [OH-] = 1.0×10^{-5}M
- Since the solution is buffered, the **[OH-] at equilibrium will also be 1 x 10^{-5} M**

$Ksp = 1.8 \times 10^{-11} = [Mg^{2+}]*[OH-]^2$

$1.8 \times 10^{-11} = [Mg^{2+}]*[1.0 \times 10^{-5}]^2$

[Mg2+] = 0.18M

Consider the dissolution of CaF2:

CaF_2(s) ⇔ Ca2+(*aq*) + 2F-(*aq*)
- The F-(*aq*) ion is a weak base and can combine with H+(*aq*) to produce the weak acid HF:

F-(*aq*) + H+(*aq*) ⇔ HF(*aq*)
- In aqueous solution, therefore, the overall (balanced) equation for the dissolution of CaF2(s) would consist of two consecutive reactions whose net reaction would be:

CaF_2(s) + 2H+(*aq*)⇔ Ca2+(*aq*) + 2HF(*aq*)
- Thus, from Le Chatelier's principle, as the [H+] increases (i.e. *as pH decreases*) the reaction is driven to the right (more of the solid dissolves)

In both of the above cases (i.e. $Mg(OH)_2$ and CaF_2) we have seen that solubility increases with increasing [H+] (decreasing pH)
- In both cases the solid dissolves to produce *an anion that is basic* in nature. Increasing the [H+] essentially removes the free anion from solution by forming the weak acid. This drives the reaction to the right and more solid dissolves.

The solubility of slightly soluble salts containing basic anions increases as [H+] increases (as pH is reduced)
- The more basic the anion, the more pronounced the effect

3) **Formation of Complex Ions**

Metal ions characteristically act as Lewis acids towards H2O(*l*)

- They accept a non-bonding pair of electrons from H2O(*l*) which behaves as a Lewis base
- Other compounds can act as Lewis bases towards metal ions
    - Such interactions can affect the solubility of the metal ion

AgCl(s) has a low solubility in H_2O(*l*), but can be solubilized in H_2O(*l*) with the addition of ammonia (NH3)

AgCl(s) ⇔ ~~Ag+(*aq*)~~ + Cl-(*aq*)

~~Ag+(*aq*)~~ + $2NH_3$(*aq*) ⇔ $Ag(NH_3)_2^+$ (*aq*)

AgCl(s) + $2NH_3$(*aq*) ⇔ $Ag(NH_3)_2$+(*aq*) + Cl-(*aq*)

- The presence of NH_3(*aq*) will drive the dissolution of AgCl(s) because it effectively removes free Ag+(*aq*) ions from solution (thus, the top reaction above is driven to the right by Le Chatelier's principle)

The metal ion is hydrated (surrounded, separated and dispersed) by H_2O(*l*) molecules
- In order for the NH_3(*aq*) molecules to act as a Lewis base with the metal ions, they must have a greater affinity for the metal ion than do the H_2O(*l*) molecules
- An assembly of a metal ion and the Lewis bases bonded to it, is called a ***complex ion***

☐ The stability of a complex ion can be judged by the magnitude of the equilibrium constant for its formation

$$K_f = \frac{\left[Ag(NH_3)_2^+\right]}{\left[Ag^+\right]\left[NH_3\right]^2} = 1.7 \times 10^7$$

What is the concentration of Ag+(*aq*) in a 0.01M solution of $AgNO_3$(s) at equilibrium if NH_3(*aq*) is added to give an equilibrium concentration of NH_3(*aq*) of 0.20M. Don't worry about any volume change when the ammonia is added. The equilibrium equation for the formation of the complex ion of Ag+(*aq*) with NH_3(*aq*) is:

Ag+(*aq*) + $2NH_3$(*aq*) ⇔ $Ag(NH_3)_2$+(*aq*)

And

$Kf = 1.7 \times 10^7$

- The concentration of Ag+(*aq*) at equilibrium = XM
- The concentration of NH3(*aq*) at equilibrium is given as 0.20M

What about the equilibrium concentration of $Ag(NH_3)_2$+(*aq*)?

- Kf is fairly large. Therefore, NH_3(*aq*) will be quite effective at removing the Ag+(*aq*) ion. Since we have an excess of NH_3(*aq*) compared to $AgNO_3$(s) we can assume that almost all of the $AgNO_3$(s) will be converted to either Ag+(s) or complex ion
- Thus, at equilibrium the concentration of $Ag(NH_3)_2$+(*aq*) = (0.01 - X)M

$$K_f = \frac{(0.01 - X)}{(X)(0.20)^2} = 1.7 \times 10^7$$

$6.8 \times 10^5 X + X = 0.01$

$6.8 \times 10^5 X \sim 0.01$

$X = 1.47 \times 10^{-8}$ M

The presence of $NH_3(aq)$, and the formation of the complex ion with Ag+(aq), significantly reduces the equilibrium concentration of Ag+(aq) ion, and thus drives the dissolution of $AgNO_3(s)$

Precipitation and Separation of Ions

Will a precipitate form when 0.15L of 2.5×10^{-3} M of $Pb(NO_3)_2$ is added to 0.2L of 4.0×10^{-3} M of Na_2SO_4? Ksp for $PbSO_4 = 1.6 \times 10^{-8}$

PbSO4(s) ⇔ Pb2+(*aq*) + SO42-(*aq*)

Ksp = [Pb2+] * [SO42-] = 1.6 x 10-8 at equilibrium

Let's solve for the ***ion product***, Q:

Q = [Pb2+] * [SO42-] at the starting concentrations

What are the starting concentrations?

- The total volume will be 0.15L + 0.2L = 0.35L
- The total amount of Pb2+ ion = (0.15L)*2.5 x 10-3moles/L = 3.75 x 10-4 moles
- ☐ Thus the initial molar concentration of Pb2+ = 3.75 x 10-4 moles/0.35L = **1.07 x 10-3M**

- The total amount of SO42- ion = (0.20L)*4.0 x 10-3moles/L = 8.0 x 10-4 moles
- ☐ Thus the initial molar concentration of SO42- ion = 8.0 x 10-4 moles/0.35L = **2.29 x 10-3M**

Therefore:

Q = 1.07 x 10-3M * 2.29 x 10-3M = **2.45 x 10-6**

Q > Ksp

Therefore, ***precipitation of PbSO4 will occur when the solutions are mixed***

And as a result, Pb2+ and SO42- ions are "selectively removed" from solution due to this precipitation