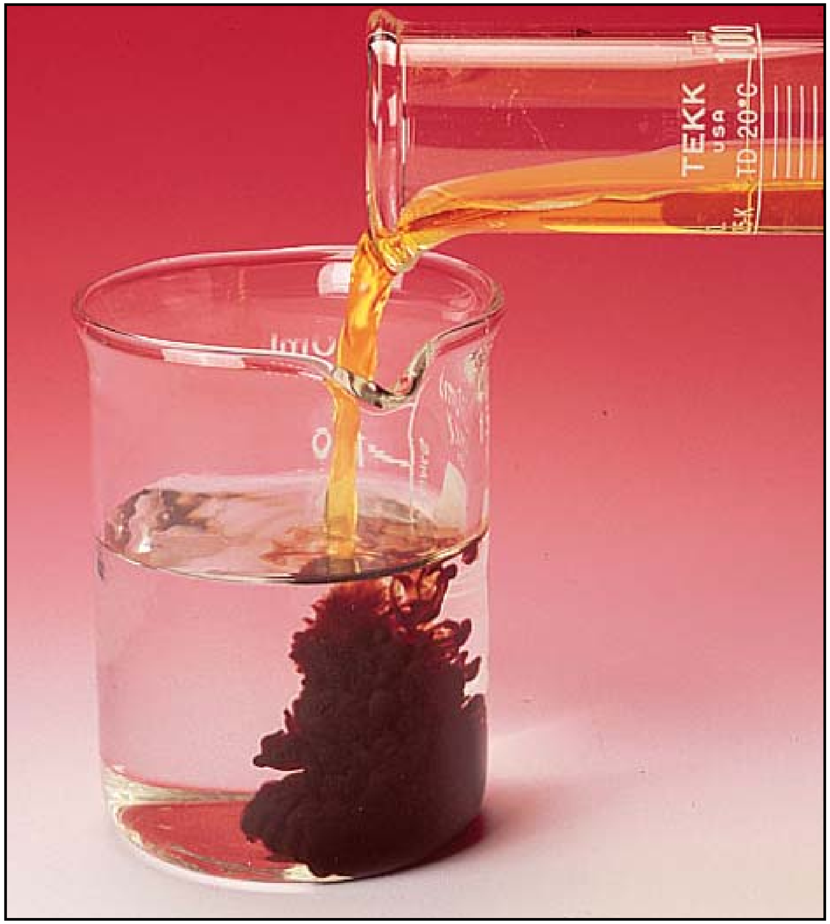
Insoluble Salts (Precipitates)

- Zumdahl Section 8.8
- Great examples of Heterogeneous Equilibrium.
- Ions and salts that are only sparingly soluble in water.
- What Solubility (S=X) is.
- How to ppt valuable ions (Ag, Au, Pt etc).
- Two classic applications of NICE table, and chemical equilibrium.
- Problems Ch 8: 82-87, 91, 96, 98, 99.

Precipitate of Bismuth Sulfide (Bi_2S_3)



$(NH_4)_2S$(aq) in solution and $Bi(NO_3)_3$ (aq) poured in to form the ppt

The ppt of a salt is the reverse direction of the solubility of the solid salt.

$$Bi_2S_3(s) \rightleftarrows 2Bi^{3+} + 3S^{2-}$$

Precipitation does NOT go to completion and some Bi^{3+} and S^{2-} ions will remain in solution, (has solubility) controlled by an equilibrium.

Solubility and Equilibrium Constant

Salt	K_{sp}	Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

What is the connection between the Solubility of a solid salt and its equilibrium constant, called K_{SP} (SP for Solubility Product)?

The solubility is the maximum amount of salt that will go into solution, whether or not it forms ions.

The K_{SP} is the Equilib. Cnst. For the ionization process.

Ag_2S example of solubility

Salt	K_{sp}	Solubility (mol/L)
Ag_2S	1.6×10^{-49}	3.4×10^{-17}

$$Ag_2S(s) \rightleftarrows 2Ag^+(aq) + S^{2-}(aq)$$

The K_{SP} is for this reaction. Let us write out Q and the NICE table.

$$Q = \frac{a_{Ag^+}^2 \cdot a_{S^{2-}}}{a_{Ag_2S}} \quad and \;\; a_{Ag_2S} = 1 \; and \;\; a_{S^{2-}} = \frac{\left[S^{2-}\right]}{1M}$$

$$Q_{SP} = \frac{\left[Ag^+\right]^2 \cdot \left[S^{2-}\right]}{1} = \left[Ag^+\right]^2 \cdot \left[S^{2-}\right]$$

Ag_2S example NICE Table

$$Ag_2S(s) \rightleftarrows 2Ag^+(aq) + S^{2-}(aq)$$

The Solubility (S=X) is the amount of salt in the solution whether it ionized or not. Assume we start with unionized salt (concentration S) and it completely ionizes at equilibrium.

Species	$Ag_2S(s)\dagger$	$Ag^+(aq)$	$S^{2-}(aq)$
Initial	$[Ag_2S]_o$	0	0
Change	$-S$	$2S$	S
New	$[Ag_2S]_o - S$	$2S$	S

$$Q_{@Eq} = \left[Ag^+\right]^2 \cdot \left[S^{2-}\right] = (2S)^2 \cdot S = K_{SP}$$

The amount S represents what was used from the solid that is not in the liquid, but surrounded by it. The New conditions must still have some solid salt present or the system will not equilibrate at K_{SP}.

Ag_2S example NICE Table

Ag_2S	1.6×10^{-49}	3.4×10^{-17}

$$Ag_2S(s) \rightleftarrows 2Ag^+(aq) + S^{2-}(aq)$$

The Solubility (S=X) is the amount of salt in the solution whether it ionized or not. Salt completely ionizes equilibrium. There must be some solid salt in the bottom of the beaker to ensure you have saturated the solution, otherwise $Q<K_{SP}$.

$$Q_{SP} = \left[Ag^+\right]^2 \cdot \left[S^{2-}\right] = (2S)^2 \cdot S = K_{SP}$$

$$4S^3 = 1.6 \cdot 10^{-49} \Rightarrow S = 3.4 \cdot 10^{-17} M$$

If 10 grams of Ag_2S are put into 1 liter of water, will the solution be saturated?

Ag_2S example NICE Table

Ag_2S	1.6×10^{-49}	3.4×10^{-17}

$$Ag_2S(s) \rightleftarrows 2Ag^+(aq) + S^{2-}(aq)$$

If 2 nano-grams of Ag_2S are put into 300 million liters of water, will the solution be saturated?

$$C_{Ag_2S} = \frac{2\cdot 10^{-9} g}{300\cdot 10^{6} \ell} \frac{1}{M_{W,Ag_2S}} = 6.6\cdot 10^{-18} M = X < S$$

$$Q = \left[Ag^+\right]^2 \cdot \left[S^{2-}\right] = (2X)^2 \cdot X = 1.1\cdot 10^{-51} < K_{SP}$$

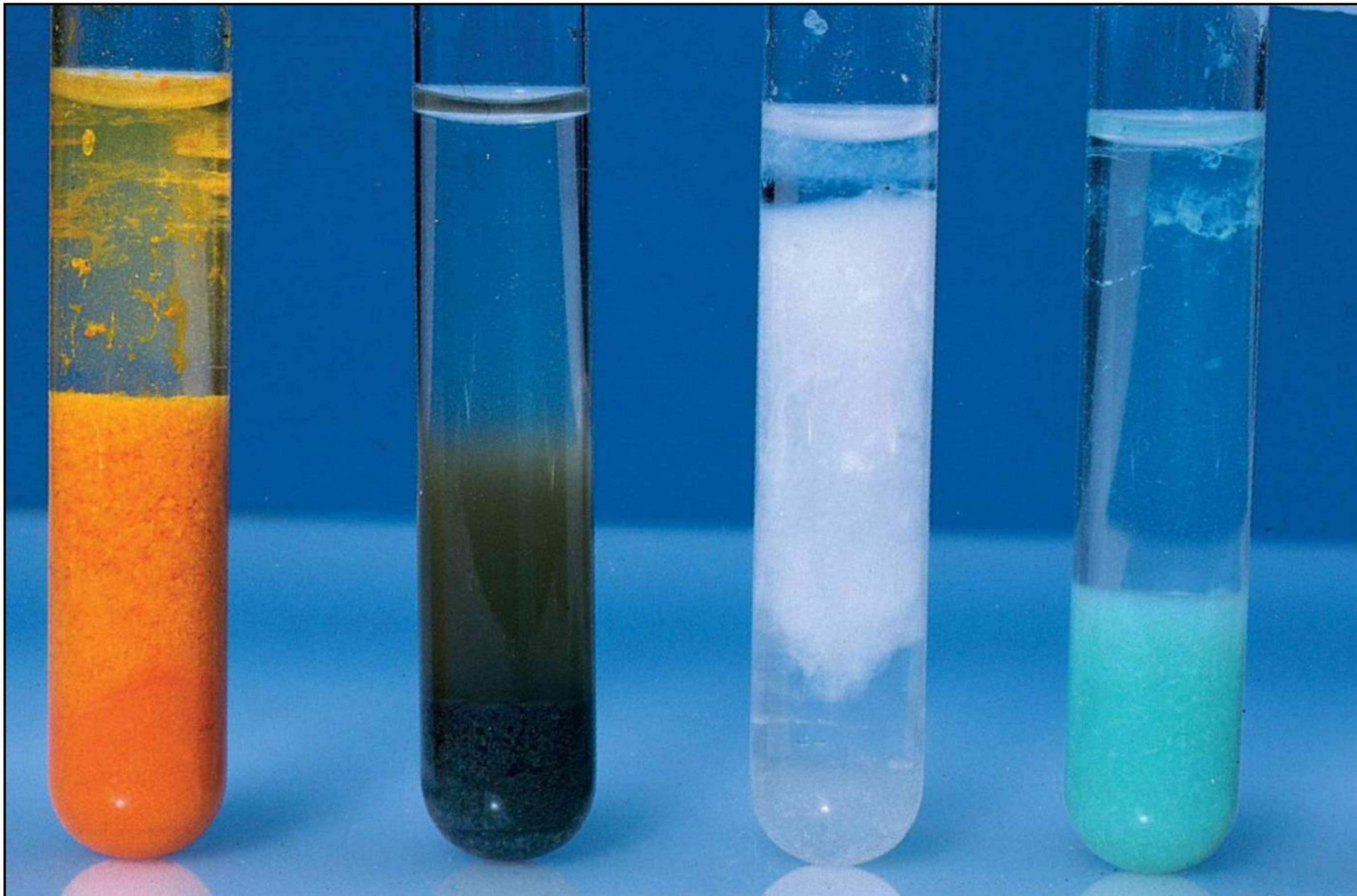
If 10 grams of Ag_2S are put into 3 liters of water, will the solution be saturated?

$$C_{Ag_2S} = \frac{10g}{3\ell} \frac{1}{M_{W,Ag_2S}} = 0.0134M = X$$

$$Q = \left[Ag^+\right]^2 \cdot \left[S^{2-}\right] = (2X)^2 \cdot X = 4\cdot 0.0134^3 = 9.6\cdot 10^{-6} >> K_{SP}$$

Almost none of it will dissolve, the Solubility will max out a 3.4e-17 M

Cadmium Sulfide; Chromium(III) Hydroxide; Aluminum Hydroxide; Nickel(II) Hydroxide



Examples of Precipitates

Gastrointestinal X ray with Barium Sulfate

$Ba(SO_4)$ is not very soluble; you drink a "milkshake" with it in it.

Ba is a heavy metal and scatters X-rays very efficiently.

Ba^{2+} ion is a poison, but, because salt is insoluble it does not pass through the gut.

Two examples relating S and K_{SP}

$$BaS(s) \rightleftarrows 1Ba^{+2}(aq) + 1S^{2-}(aq)$$

A Salt (of metal and non-metal) ionize. Electrical neutrality happens because the solid is neutral and the charges must be conserved:

$$2 \cdot \left[Ba^{+2}\right] = 2 \cdot \left[S^{2-}\right]$$

At equilibrium the solubility is related to the KSP as:

$$K_{SP} = Q_{SP@Eq} = \left[Ba^{2+}\right]^1 \cdot \left[S^{2-}\right]^1$$

$$K_{SP} = (1S)^1 (1S)^1 = S^{(2)}$$

Notice that the final connection between the K_{SP} and S is through the stoichiometric coefficients (SCs) and not the actual charges on the ions. Consider BaS, where the charges are 2, but the SCs are 1. K=S^2

Try it for Ca3(PO4)2 next.

Second Example relating S and K_{SP}

$$Ca_3(PO_4)_2(s) \rightleftarrows 3Ca^{+2}(aq) + 2(PO_4)^{3-}(aq)$$

A Salt Dissociates: Electrical neutrality happens because the solid is neutral and the charges must be conserved:

$$2 \cdot \left[Ca^{+2}\right] = 3 \cdot \left[(PO_4)^{3-}\right]$$

$$NICE\ Table: \quad \left[Ca^{+2}\right] = 3 \cdot S \text{ and } \left[(PO_4)^{3-}\right] = 2 \cdot S$$

At equilibrium the solubility is related to the K_{SP} as:

$$K_{SP} = Q_{SP@Eq} = \left[Ca^{+2}\right]^3 \cdot \left[(PO_4)^{3-}\right]^2$$

$$K_{SP} = (3S)^3(2S)^2 = \left\{3^3 2^2\right\} S^{(5)} = 36 \cdot S^5$$

The connection between the K_{SP} and S is through the stoichiometric coefficients (SCs) and not the actual charges on the ions.

The General Case, and Electrical Neutrality

$$M_{\nu_m} N_{\nu_n}(s) \rightleftarrows \nu_m M^{+m}(aq) + \nu_n N^{-n}(aq)$$

A metal (M) and a non-metal (N) ionize to form the +m metal ion and the –n nonmetal ion (could be an oxyanion like NO_3^- or CO_3^{2-} where n=1 and =2 respectively). Electrical neutrality of the solution happens because:

$$\nu_m \cdot m = \nu_n \cdot n$$

The solubility is the number of moles in solution as a solid, S. But the solid only exists as fully dissociated ions. $\left[M^{+m}\right] = \nu_m S$ and $\left[N^{-n}\right] = \nu_n S$

At equilibrium the solubility is related to the K_{SP} as:

$$Q_{SP} = \left[M^{+m}\right]^{\nu_m} \cdot \left[N^{-n}\right]^{\nu_n}$$

$$K_{SP} = (\nu_m S)^{\nu_m} (\nu_n S)^{\nu_n} = \left\{(\nu_m)^{\nu_m} (\nu_n)^{\nu_n}\right\} S^{(\nu_m + \nu_n)}$$

Notice that the final connection between the K_{SP} and S is through the stoichiometric coefficients (SCs) and not the actual charges on the ions.

Relative Solubilites.

Can one compare KSPs and get relative solubilities?

Only if the stoichiometric coefficients are the same. Eg yes you can compare   AgCl and BaS K's to determine which is more soluble.

But if the coefficients are quite different one cannot. Eg   AgCl and $Ag_3(PO_4)$ the K_{sp} (AgCl) > $K_{sp}(Ag_3(PO_4))$, but the solubility is the other way around.

$$Q_{SP} = \left[M^{+m}\right]^{\nu_m} \cdot \left[N^{-n}\right]^{\nu_n}$$

$$K_{SP} = \left(\nu_m S\right)^{\nu_m} \left(\nu_n S\right)^{\nu_n} = \left\{\left(\nu_m\right)^{\nu_m} \left(\nu_n\right)^{\nu_n}\right\} S^{\left(\nu_m + \nu_n\right)}$$

$$K_{SP}\left(AgCl\right) = 1.6 \cdot 10^{-10} = S^2 \Rightarrow S = 1.3 \cdot 10^{-5}$$

$$K_{SP}\left(Ag_3\left(PO_4\right)\right) = 1.8 \cdot 10^{-18} = 9S^4 \Rightarrow S = 2.3 \cdot 10^{-4}$$

Get Numbers from Table of Solubility Constants (K_{SP})

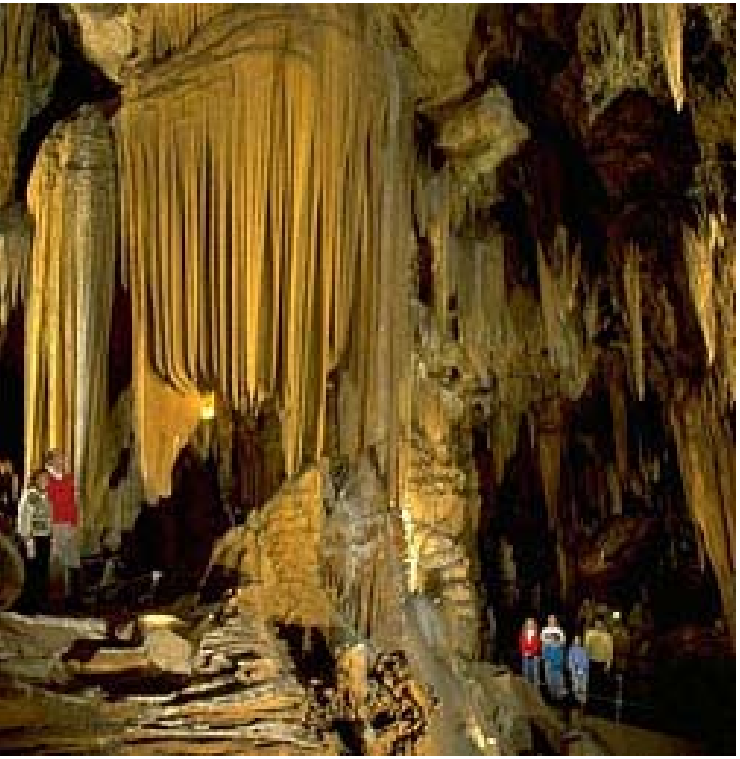
K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)
Fluorides	
BaF_2	2.4×10^{-5}
MgF_2	6.4×10^{-9}
PbF_2	4×10^{-8}
SrF_2	7.9×10^{-10}
CaF_2	4.0×10^{-11}
Chlorides	
$PbCl_2$	1.6×10^{-5}
$AgCl$	1.6×10^{-10}
Hg_2Cl_2*	1.1×10^{-18}
Bromides	
$PbBr_2$	4.6×10^{-6}
$AgBr$	5.0×10^{-13}
Hg_2Br_2*	1.3×10^{-22}
Iodides	
PbI_2	1.4×10^{-8}
AgI	1.5×10^{-16}
Hg_2I_2*	4.5×10^{-29}
Sulfates	
$CaSO_4$	6.1×10^{-5}
Ag_2SO_4	1.2×10^{-5}
$SrSO_4$	3.2×10^{-7}
$PbSO_4$	1.3×10^{-8}
$BaSO_4$	1.5×10^{-9}
Chromates	
$SrCrO_4$	3.6×10^{-5}

Ionic Solid	K_{sp} (at 25°C)
Hg_2CrO_4*	2×10^{-9}
$BaCrO_4$	8.5×10^{-11}
Ag_2CrO_4	9.0×10^{-12}
$PbCrO_4$	2×10^{-16}
Carbonates	
$NiCO_3$	1.4×10^{-7}
$CaCO_3$	8.7×10^{-9}
$BaCO_3$	1.6×10^{-9}
$SrCO_3$	7×10^{-10}
$CuCO_3$	2.5×10^{-10}
$ZnCO_3$	2×10^{-10}
$MnCO_3$	8.8×10^{-11}
$FeCO_3$	2.1×10^{-11}
Ag_2CO_3	8.1×10^{-12}
$CdCO_3$	5.2×10^{-12}
$PbCO_3$	1.5×10^{-15}
$MgCO_3$	1×10^{-15}
Hg_2CO_3*	9.0×10^{-15}
Hydroxides	
$Ba(OH)_2$	5.0×10^{-3}
$Sr(OH)_2$	3.2×10^{-4}
$Ca(OH)_2$	1.3×10^{-6}
$AgOH$	2.0×10^{-8}
$Mg(OH)_2$	8.9×10^{-12}
$Mn(OH)_2$	2×10^{-13}
$Cd(OH)_2$	5.9×10^{-15}
$Pb(OH)_2$	1.2×10^{-15}
$Fe(OH)_2$	1.8×10^{-15}

Ionic Solid	K_{sp} (at 25°C)
$Co(OH)_2$	2.5×10^{-16}
$Ni(OH)_2$	1.6×10^{-16}
$Zn(OH)_2$	4.5×10^{-17}
$Cu(OH)_2$	1.6×10^{-19}
$Hg(OH)_2$	3×10^{-26}
$Sn(OH)_2$	3×10^{-27}
$Cr(OH)_3$	6.7×10^{-31}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}
$Co(OH)_3$	2.5×10^{-43}
Sulfides	
MnS	2.3×10^{-13}
FeS	3.7×10^{-19}
NiS	3×10^{-21}
CoS	5×10^{-22}
ZnS	2.5×10^{-22}
SnS	1×10^{-26}
CdS	1.0×10^{-28}
PbS	7×10^{-29}
CuS	8.5×10^{-45}
Ag_2S	1.6×10^{-49}
HgS	1.6×10^{-54}
Phosphates	
Ag_3PO_4	1.8×10^{-18}
$Sr_3(PO_4)_2$	1×10^{-31}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$Ba_3(PO_4)_2$	6×10^{-39}
$Pb_3(PO_4)_2$	1×10^{-54}

Stalactites, Stalagmites and Coral



In basic solution, lots of OH^- ions, the bicarbonate ion shifts equilibrium to form carbonate, which can ppt as $CaCO_3$.

$$CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

Coral and Stalactites and Stalagmites

The reaction that destroys coral and stalactites, and marble statues is: $H^{+}(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + HCO_3^{-}(aq)$

What is the K for this reaction and what is the significance of its value regarding the effect of acid on coral stability?

$$HCO_3^{-}(aq) \rightarrow H^{+}(aq) + CO_3^{2-}(aq) \quad K_{A_2} = 4.8 \cdot 10^{-11}$$

$$CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + CO_3^{2-}(aq) \quad K_{SP} = 8.7 \cdot 10^{-9}$$

Alive

Dead

$$CO_2(g) + H_2O(aq) \rightleftarrows H_2CO_3(aq) \rightarrow H^{+}(aq) + HCO_3^{-}(aq)$$

Stalactites, Statues and Coral

However, in acid solution (eg add HCl) the acid H^+ competes with the carbonate to make bicarbonate, and this dissolves the stalagmites.

Acid makes Bicarbonate; Therefore $CaCO_3$ (coral) dissolves.

$$H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$$

$$H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq)$$

The presence of acid upsets the balance for coral who cannot make the hard $CaCO_3$ shell and therefore die. The presence of acid in the water is increased by CO_2 in the air.

$$CO_2(g) + H_2O(aq) \rightleftarrows H_2CO_3(aq) \rightarrow H^+(aq) + HCO_3^-(aq)$$

In the last 20 years, acid concentration in the oceans has increased by 40%.

Mix Two Salts Together

- We did this before, but then we assumed reactions went to completion.
- Now for sparingly soluble salts the reaction does not quite go to completion and we find an equilibrium for every salt even the ones that ppt.
- Combine our skills of reactions in solution with the equilibrium constants.
- Apply these two aspects of the reactions to specific problems.
- Mix $AgNO_3$ and NH_4Cl solutions together. What are the concentrations of each of the ions at the end and how much salt (by moles/mass) ppt out?

Mix Two Salts; Ppt AgCl

- Mix 50 mls 0.01M $AgNO_3$ and 30 mls .05M NH_4Cl solutions together. If no ppt what is the concentration of each ion in solution?

$$\left[Ag^{+}\right] = 0.01\frac{50}{80} = 0.00625$$

$$\left[Cl^{-}\right] = 0.05\frac{30}{80} = 0.0188M$$

$$Net\ Rxn: Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s) \qquad K_{SP} = 1.6\cdot 10^{-10}$$

Lots of different strategies from here. A) Solve it from here; B) Go to completion and then solve from there. Either way gets the same answer.

Mix Two Salts; Ppt AgCl

- Using method B: The limiting reactant is the silver ion. So 0.00625 M Ag^+ ppt, taking 0.00625 M Cl^- with it.
- Leaving, as new initial conditions:

$$\left[Ag^+\right] = 0.00625 - 0.00625 = 0M$$

$$\left[Cl^-\right] = 0.0188 - 0.00625 = 0.0125M$$

$$\left[AgCl\right] = 0.00626M\,\dagger$$

$$n_{AgCl} = 0.00626M \cdot 0.080l = 5.00 \cdot 10^{-4}\,moles$$

† The “concentration” of AgCl(s) represents the initial accessible amount of AgCl, some of which will redissolve as ions, the rest will ppt. as moles of AgCl(s). .

Re-Dissolve AgCl (Chloride is the common ion)

- The new initial conditions are:

$$\left[Ag^{+}\right]=0M \quad \left[Cl^{-}\right]=0.0125M$$

- The NIC table now:

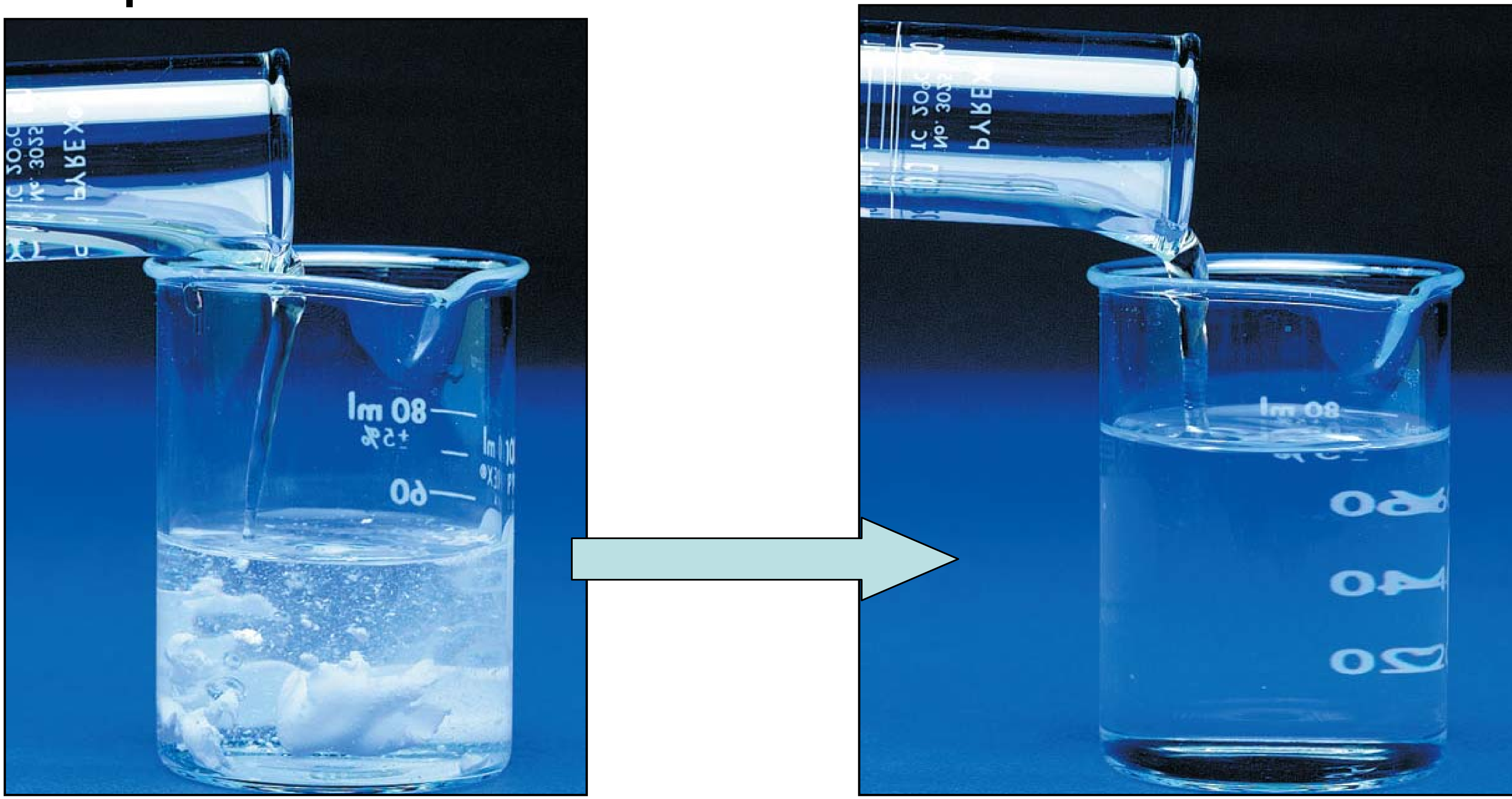
$Species$	$AgCl(s)$	$Ag^{+}(aq)$	$Cl^{-}(aq)$
$Initial$	0.00626	0	0.0125
$Change$	$-X$	X	X
New	$0.00626-X$	X	$0.0125+X$

- Equilibrium Expression

$$K_{SP}=1.6\cdot 10^{-10}=\left[Ag^{+}\right]\left[Cl^{-}\right]=X\cdot(0.0125+X)$$

$$X\approx\frac{1.6\cdot 10^{-10}}{0.0125}=1.3\cdot 10^{-8}M\left(Ag^{+}(aq)\right)$$

Aqueous Ammonia Added to Silver Chloride



$$AgCl(s) + NH_3(aq) \rightleftarrows Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)$$

What is the solubility of AgCl in 10M aqueous ammonia given K for this reaction?

$$K_C = 2.8 \cdot 10^{-3}$$