

Today

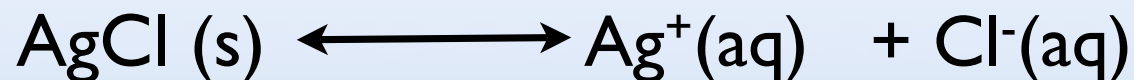
Solubility

The easiest of all the equilibria

Equilibria with no approximations

How to set up such a problem

Solubility Equilibria



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

Molar solubility

How many moles per L of solution at equilibrium

Solubility

How many grams per L of solution at equilibrium

What is the solubility of ScF_3 ?



$$K_{\text{sp}} = [\text{Sc}^{3+}][\text{F}^{-}]^3 = 4.2 \times 10^{-18}$$

	ScF_3	Sc^{3+}	F^{-}	$K = [\text{Sc}^{3+}][\text{F}^{-}]^3$
I	n_{solid}	0	0	$K = (x)(3x)^3$
C	-x	+x	+3x	$K = 27x^4 = 4.2 \times 10^{-18}$
E	n-x	+x	+3x	$x = 1.99 \times 10^{-5}$

$$x = [\text{Sc}^{3+}]$$

x is also the number of moles of ScF_3 that dissolve
molar solubility 1.99×10^{-5} moles/L
solubility 2×10^{-3} g/L

Selective precipitation

I have a solution which contains
0.1 M AgNO_3 and 0.1 M PbNO_3 .

How can I get out the silver and leave the lead behind?

Add an anion for an insoluble salt for silver such as Cl^-

K_{sp} is 1.6×10^{-10} for AgCl

But PbCl_2 is also insoluble so it will precipitate out as well

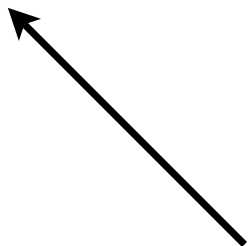
K_{sp} is 2.4×10^{-4} for PbCl_2

The K_{sp} for AgCl is much smaller so we can selectively precipitate the AgCl

I have a solution which contains
0.1 M AgNO_3 and 0.1 M PbNO_3 .
How can I get out the silver and leave the lead behind?

what is the maximum concentration of Cl^-
we can have and still have the PbCl_2 dissolved $K_{sp} = 2.4 \times 10^{-4}$

- A. $4.9 \times 10^{-2} \text{ M}$
- B. $1.2 \times 10^{-4} \text{ M}$
- C. $2.4 \times 10^{-4} \text{ M}$
- D. $2.4 \times 10^{-3} \text{ M}$

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$
$$[\text{Cl}^-] = \sqrt{K_{sp}/[\text{Pb}^{2+}]}$$
$$[\text{Cl}^-] = \sqrt{2.4 \times 10^{-3}}$$


I have a solution which contains
0.1 M AgNO_3 and 0.1 M PbNO_3 .
How can I get out the silver and leave the lead behind?

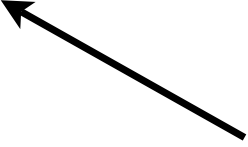
If the Cl^- concentration is 4.9×10^{-2} M, what is the Ag^+ concentration?
 $K_{\text{sp}} = 1.6 \times 10^{-10}$ for AgCl

A. 4.9×10^{-12} M

B. 3.2×10^{-9} M

C. 1.6×10^{-10} M

D. 2.4×10^{-3} M

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$
$$[\text{Ag}^+] = (K_{\text{sp}}/[\text{Cl}^-])$$
$$[\text{Ag}^+] = (1.6 \times 10^{-10}) / (4.9 \times 10^{-2})$$


Previously solving acid base problems

Strong acids

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

Weak acids

$$[\text{H}^+] = (K_a C_a)$$

Buffer

$$[\text{H}^+] = K_a (C_a / C_b)$$

Polyprotic (inbetween)

$$[\text{H}^+] = \text{sqrt}(K_{a1} K_{a2})$$

All of these involve some kind of approximation

First we ignore that there is any H^+ for the water (ignore K_w except when relating OH^-)

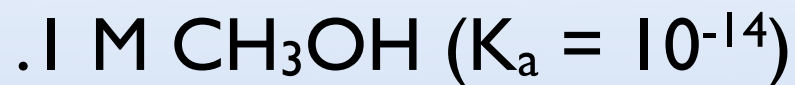
Next we assume the concentration of acid is large
 $C_a > 10^{-2}$ and that K_a is small

For polyprotics we assume the K 's are well separated

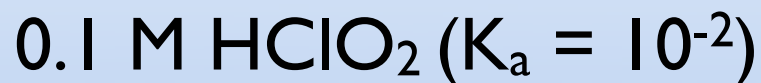
When will this fail



too dilute



K_a too close to K_w



K_a too large

What to do?

It is all simply a very large algebra problem

The key: Setting up the problem

What is the pH of 10^{-8} M HCl?

- A. 8
- B. 7
- C. a little less than 7
- D. a little more than 7

water starts at 10^{-7} M H^+ from K_w
adding a very tiny tiny bit of acid will
make it only slightly acidic

We can solve this problem exactly

What we need is a set of equations

What are our unknowns?

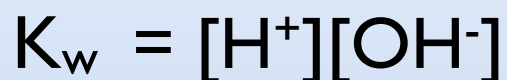
The concentrations in the solution

$[H^+]$ $[Cl^-]$ $[OH^-]$

Three unknowns
We need 3 equations

In any equilibrium problems we will have three types of equations that relate the concentrations to known quantities (equilibrium constants, starting concentrations...)

Type I: Equilibrium Constant Equation



Type II: Mass Balance

$C_{\text{HCl}} = [\text{Cl}^-]$ all of the Cl^- comes from the HCl

Type II: Charge Balance (solutions are neutral in charge)



sum of all positive charges equals
sum of all negative charges

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

$$C_{\text{HCl}} = [\text{Cl}^-]$$

Three equations and three unknowns
(I know K_w and C_{HCl})

Now it is just algebra

Weak Acid Problem (no approximations)

Unknowns



Need four equations

Mass Balance

$$C_{\text{HA}} = [\text{HA}] + [\text{A}^-]$$

Charge Balance

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

2 Equilibria

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

$$K_w = [\text{H}^+][\text{OH}^-]$$

Some Algebra and then

$$[\text{H}^+]^3 + K_a[\text{H}^+]^2 - (K_w + K_a C_{\text{HA}})[\text{H}^+] - K_a K_w = 0$$

Exact solution for the $[\text{H}^+]$ for a weak acid

If we say $K_w \sim 0$ then we can write this as

$$[\text{H}^+]^2 + K_a([\text{H}^+] - C_{\text{HA}}) = 0$$

If we say $C_{\text{HA}} \gg \text{H}^+$ then

$$\begin{aligned} [\text{H}^+]^2 - K_a C_{\text{HA}} &= 0 \\ [\text{H}^+] &= \text{sqrt}(K_a C_{\text{HA}}) \end{aligned}$$

Let's look at the equations we would need for finding the pH of a solution of 0.1 M NaH_2PO_4