Today

Solubility

The easiest of all the equilibria

Equilibria with no approximations

How to set up such a problem

Solubility Equilibria

$$AgCl\,(s) \longleftrightarrow Ag^{+}(aq) + Cl^{-}(aq)$$

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

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?

$$ScF_3\ (s) \longleftrightarrow Sc^{3+}(aq) + 3F^{-}(aq)$$

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

	ScF_3	Sc^{3+}	F^{-}
I	n_{solid}	0	0
C	-x	+x	+3x
E	n-x	+x	+3x

$$K = [Sc^{3+}][F^{-}]^3$$

$$K = (x)(3x)^3$$

$$K = 27x^4 = 4.2 \times 10^{-18}$$

$$x = 1.99 \times 10^{-5}$$

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

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. 4.9×10^{-2} M

B. 1.2×10^{-4} M

C. 2.4×10^{-4} M

D. 2.4×10^{-3} M

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

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?
$K_{sp} = 1.6 \times 10^{-10}$ 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

$$K_{sp} = [Ag^+][Cl^-]$$
$$[Ag^+] = (K_{sp}/[Cl^-])$$
$$[Ag^+] = (1.6\times10^{-10})/(4.9\times10^{-2})$$

Previously solving acid base problems

Strong acids
$[H^+] = C_a$

Weak acids
$[H^+] = (K_aC_a)$

Buffer
$[H^+] = K_a\,(C_a/C_b)$

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

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

10^{-10} M HCl — too dilute

.1 M CH_3OH ($K_a = 10^{-14}$) — K_a too close to K_w

0.1 M $HClO_2$ ($K_a = 10^{-2}$) — 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

$$K_w = [H^+][OH^-]$$

Type II: Mass Balance

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

Type II: Charge Balance (solutions are neutral in charge

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

sum or all positive charges equals
sum of all negative charges

$K_w = [H^+][OH^-]$

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

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

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

Now it is just algebra

Weak Acid Problem (no approximations)

Unknowns

$[HA]$ $[H^+]$ $[A^-]$ $[OH^-]$

Need four equations

Mass Balance

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

Charge Balance

$$[H^+] = [OH^-] + [A^-]$$

2 Equilibria

$$K_a = [H^+][A^-]/[HA] \qquad K_w = [H^+][OH^-]$$

Some Algebra and then

$$[H^+]^3 + K_a[H^+]^2 - (K_w + K_aC_{HA})[H^+] - K_aK_w = 0$$

Exact solution for the $[H^+]$ for a weak acid

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

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

If we say $C_{HA} >> H^+$ then

$$[H^+]^2 - K_aC_{HA} = 0$$

$$[H^+] = \mathrm{sqrt}(K_aC_{HA})$$

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