Today

Complex Equilibria

Approximations
when do your previous formulas fail?

In short hand notation what is dimethylamine?

A. HA

B. A^-

C. B ←

D. BH^+

Amines are like "ammonia with other substituents instead of just hydrogen

Weak Base. No Charge. B

In short hand notation what is $(CH_3)_2NH_2Cl$?

A. HA

B. A^-

C. B

D. BH^+ ←

Cl is minus
$(CH_3)_2NH_2^+$

This is a protonated amine
BH^+

In short hand notation what is potassium formate?

A. HA

B. A^- ←

C. B

D. BH^+

K^+
formate$^-$

conjugate base of formic acid

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

Saturated solution
Equilibrium solution. Solid + dissolved ions

Solubility Equilibria

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

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

What happens if we try to dissolve AgCl in a solution with NaCl in it?

What is the molar solubility of AgCl in 0.1 M NaCl?

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

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

What is the molar solubility of AgCl in 0.1 M NaCl given that $K_{sp} = 1.8 \times 10^{-10}$

$$[Ag^{+}] = K_{sp}/[Cl^{-}] = 1.8 \times 10^{-10}/0.1$$

$$[Ag^{+}] = 1.8 \times 10^{-9}$$

Ag^{+} concentration tells us how much AgCl dissolved
solubility is 1.8×10^{-9} M

This is known as the common ion effect
The effect of an ion from one compound on the solubility of another

This can be used to separate ions in solution by trying to precipitate out (from solid) the one with the lower solubility

Selective precipitation

I have a solution which contains
0.1 M $AgNO_3$ and 0.1 M $Pb(NO_3)_2$.
How can I get out the silver and leave the lead behind?

Nitrate salts are soluble so I have Ag^+ and Pb^{2+} in solution

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

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

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

We assume the K's (K_a and K_w) are well separated

What is the pH of 10^{-18} M HCl?

A. 18

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

When will this fail

10^{-10} M HCl — too dilute

0.1 M $HClO_2$ ($K_a = 10^{-2}$) — K_a too large

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

What to do?

It is all simply a very large algebra problem
The key: Setting up the problem

We can solve this problem exactly

What we need is a set of equations

What are our unknowns for the dilute HCl problem?

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

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 Ammonium Acetate

Intro to polyprotics acids

Sulfuric Acid

H_2SO_4

1st proton K_{a1} $\quad H_2SO_4 \longleftrightarrow H^+ + HSO_4^-$

2nd proton K_{a2} $\quad HSO_4^- \longleftrightarrow H^+ + SO_4^{2-}$

For sulfuric acid K_{a1} is strong (2nd is not)

What is the pH of 1 M H_2SO_4?

Sulfuric Acid

H_2SO_4

1st proton K_{a1} $\quad H_2SO_4 \longleftrightarrow H^+ + HSO_4^-$

2nd proton K_{a2} $\quad HSO_4^- \longleftrightarrow H^+ + SO_4^{2-}$

For sulfuric acid K_{a1} is strong (2nd is not)

What is the pH of 1 M H_2SO_4?

It is like the common ion effect.
Look at the second equilibrium.

Reactant	HSO_4^- $\longleftrightarrow$	H^+ +	SO_4^{2-}
Initial	1 M	1 M	0 M
Change	-x	+x	+x
Equilibrium	1-x	1+x	+x

$$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1+x)(x)}{(1-x)}$$