

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
 $(\text{CH}_3)_2\text{NH}_2\text{Cl}$?

A. HA

B. A^-

C. B

D. BH^+

Cl is minus
 $(\text{CH}_3)_2\text{NH}_2^+$

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



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

Molar solubility

How many moles per L of solution at equilibrium

Solubility

How many grams per L of solution at equilibrium

Saturated solution

Equilibrium solution. Solid + dissolved ions

Solubility Equilibria



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

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?



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

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

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

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

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 $\text{Pb}(\text{NO}_3)_2$.

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

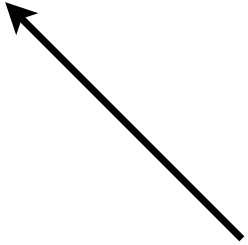
K_{sp} is 2.4×10^{-4} for PbCl_2

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 $K_{\text{sp}} = 2.4 \times 10^{-4}$

- 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. $2.4 \times 10^{-3} \text{ M}$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$
$$[\text{Cl}^-] = \sqrt{K_{\text{sp}}/[\text{Pb}^{2+}]}$$
$$[\text{Cl}^-] = \sqrt{2.4 \times 10^{-4}}$$


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

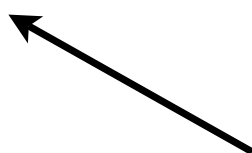
C. 1.6×10^{-10} M

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

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

Buffer

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

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 HClO₂ ($K_a = 10^{-2}$)

K_a too large

.1 M CH₃OH ($K_a = 10^{-14}$)

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?

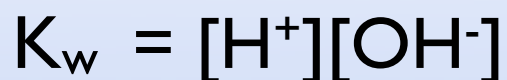
The concentrations in the solution

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

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



Type II: Mass Balance



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 Ammonium Acetate

Intro to polyprotic acids

Sulfuric Acid



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

What is the pH of 1 M H_2SO_4 ?

Sulfuric Acid



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

What is the pH of 1 M H₂SO₄?

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

Reactant	HSO ₄ ⁻	↔	H ⁺	+	SO ₄ ²⁻
Initial	1 M		1 M		0 M
Change	-x		+x		+x
Equilibrium	1-x		1+x		+x

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