

Ionic Equilibria

weak acids and bases

salts of weak acids and bases

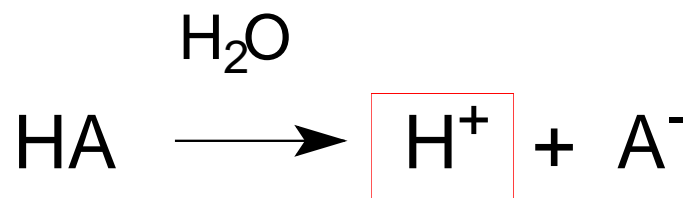
buffer solutions

solubility of slightly soluble salts

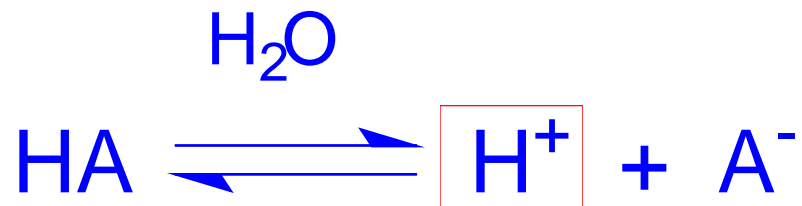
Arrhenius Definitions

produce H^+ ions in the solution

strong acids ionize completely



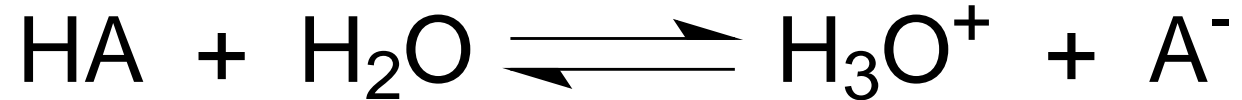
weak acids partially ionize
(equilibrium)



Bronsted Lowry Definitions

an acid is a H⁺ donor

a base is a H⁺ acceptor



Measuring acidity

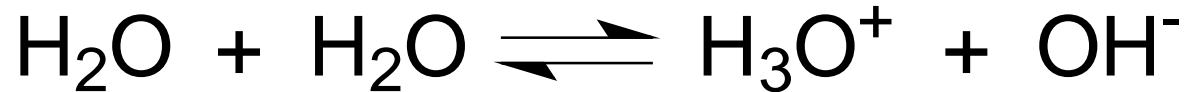
use the pH scale

$$\text{pH} = -\log[\text{H}^+]$$

or

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

Water ionizes slightly



$$K_w = 1.000 \times 10^{-14}$$

$$K_w = 1.000 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

note: pure liquids (and solids)
do not appear in equilibrium constants

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.000 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(1.000 \times 10^{-7}) \quad \text{pH} = 7.0000$$

Relationships

$$1.000 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

log of both sides

$$-14 = \log [\text{H}_3\text{O}^+] + \log [\text{OH}^-]$$

multiply by -1

$$14 = (-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-])$$

$$14 = \text{pH} + \text{pOH}$$

$$(\text{pOH} = -\log[\text{OH}^-])$$

Summary

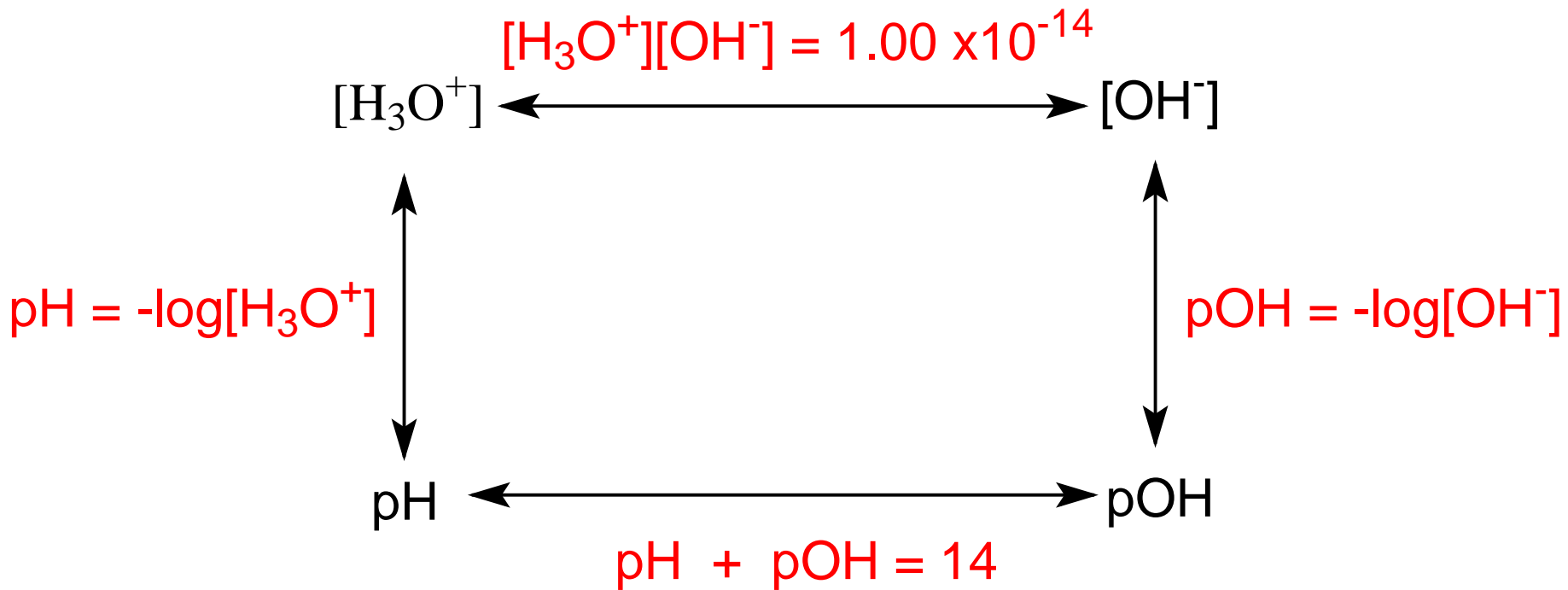
$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

Relationships



Examples

Calculate the pH of the following

$$[\text{H}_3\text{O}^+] = 2.75 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 8.243 \times 10^{-5} \text{ M}$$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+](8.243 \times 10^{-5} \text{ M}) = 1.00 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 1.213 \times 10^{-10} \text{ M}$$

Try Some

Q1

Calculate $[\text{H}_3\text{O}^+]$

$\text{pH} = 6.211$

$\text{pOH} = 9.73$

Weak Acids



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

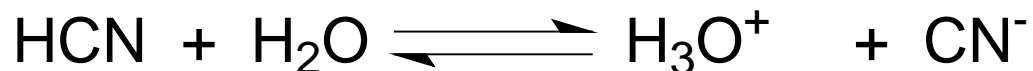
Weak Bases



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Example Problem

Calculate the pH of a 0.250M solution of HCN



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$K_a = 4.0 \times 10^{-10}$$

	HCN	H ₃ O ⁺	CN ⁻
starting amounts	0.250M	0	0
reacting			
equilibrium			

Solution

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$K_a = \frac{(x)(x)}{(0.250-x)} = \frac{x^2}{0.250-x} \quad \left. \vphantom{\frac{x^2}{0.250-x}} \right\} \text{note: a quadratic equation}$$

assume x is small compared to 0.250
(a reasonable assumption since K_a is very small ...
very few products formed at equilibrium)

$$4.0 \times 10^{-10} = \frac{x^2}{0.250}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

% Ionization

Weak acids partially ionize
(by Arrhenius definition of "weak")

$$\% \text{ ionization} = \frac{\text{amount ionized}}{\text{starting amount}} \times 100$$

From the last problem:

amount ionized = $1.0 \times 10^{-5} \text{M}$

starting amount = 0.25M

Try One

Q2

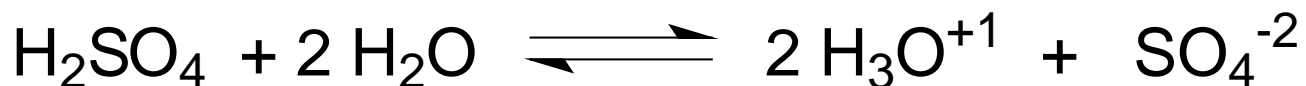
A 0.100M solution of HClO is 0.0592% ionized at equilibrium.
Calculate K_a for this acid.

Polyprotic Acids

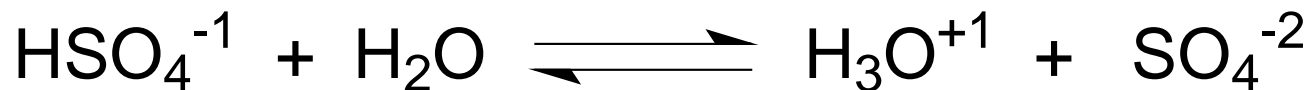
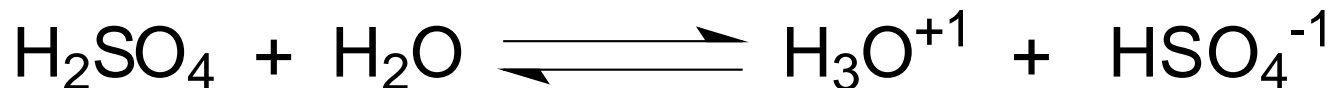
Acids with more than one "ionizable" H



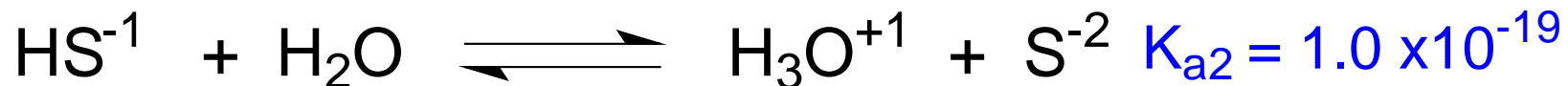
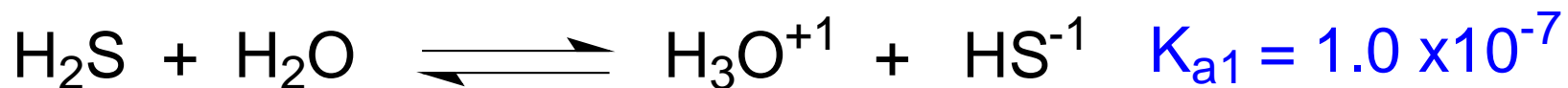
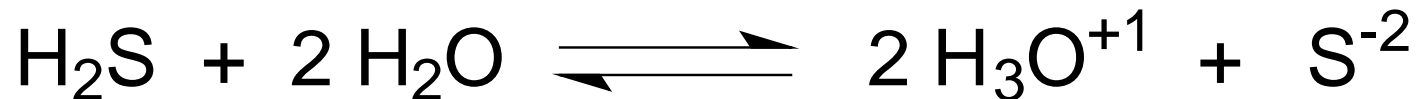
overall equation:



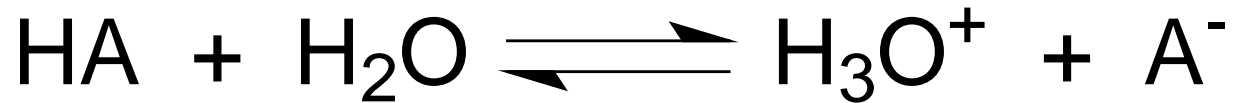
occurs in two steps



K_a and Polyprotic Acids

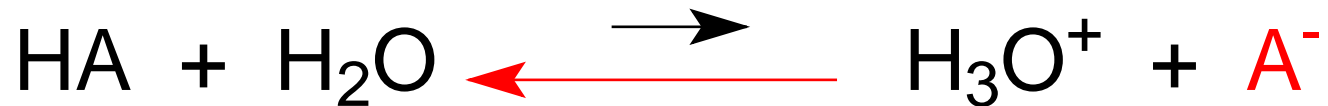


Conjugate Acids and Bases



"Weak acids form strong conjugate bases!"

If K_a is small, then the equilibrium is favored to the left.

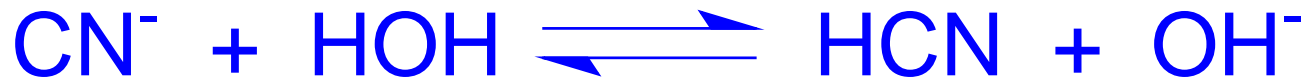


Hydrolysis

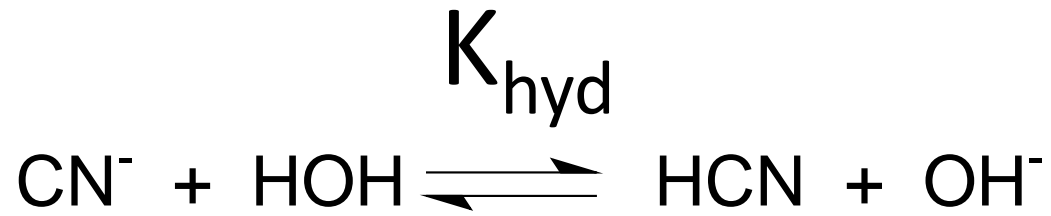
conjugates of weak acids and bases
are strong enough to react with water

K_a for the weak acid HCN is 4.0×10^{-10}

CN⁻ is the strong conjugate base of HCN



$$K_{\text{hyd}} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$



$$K_{\text{hyd}} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

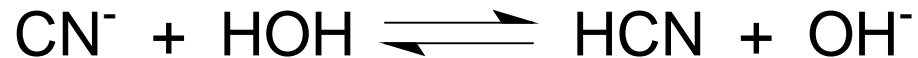
Example

Calculate the pH of a 0.25M solution of NaCN.

NaCN is a soluble ionic comp'd and ionizes completely:

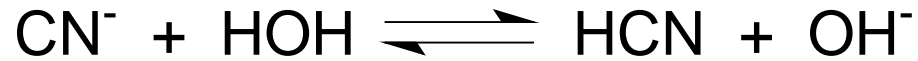


CN^- is the conjugate of a weak acid and undergoes hydrolysis



$$K_{\text{hyd}} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}}$$

Solution



	CN^-	HCN	OH^-
starting amounts	0.25M	0	0
reacting			
equilibrium			

$$K_{\text{hyd}} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

Finishing

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0025 = 2.60$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 11.40$$

Try One

Q3

Calculate the pH of a 0.150M solution of NaBrO.

K_a for HBrO is 2.50×10^{-9}

Buffer Solutions

Can stabilize pH and resist slight additions of acid or base

based on Le Chatelier's Principle

weak acid or base + salt of its conjugate

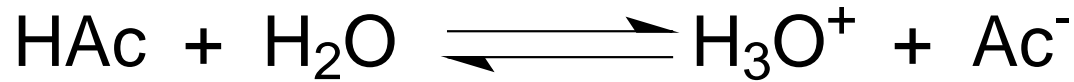
for example:

HCN and NaCN

NH₃ and NH₄Cl

A Problem to Illustrate

Calculate the pH of a solution that is 0.1000M in HAc and 0.1000M in NaAc. $K_a = 1.85 \times 10^{-5}$



$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]}$ **Note: use acid dissociation equation!**

	HAc	H ₃ O ⁺	Ac ⁻

starting			
amounts			

reacting			

equilibrium			

starting
amounts

reacting

equilibrium

Solution

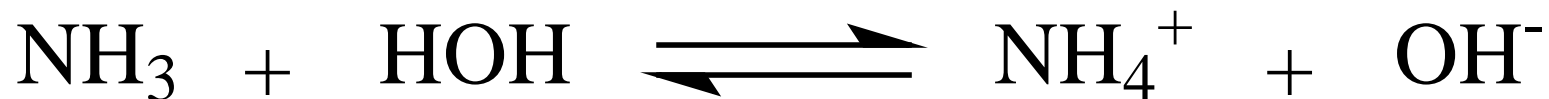
$$K_a = \frac{(x)(0.1000+x)}{(0.1000-x)}$$

assume x is small compared to 0.1000

Try One

Q4

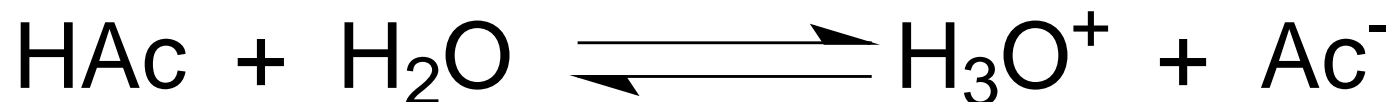
Calculate the pH of a solution made by dissolving 0.100 mol NH_3 and 0.150 mol NH_4Cl into 1.00 L solution. K_b for NH_3 is 1.80×10^{-5} .



Adding Acid to a Buffered Solution

Calculate the pH of the HAc/NaAc buffer solution (a previous problem) if 0.0100 mols HCl are added to a liter of the solution.

add 0.0100M HCl



0.1100M

0.0990M

Solution

	HAc	H ₃ O ⁺	Ac ⁻
starting amounts	0.1100M	0	0.0990M
reacting			
equilibrium			

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]}$$

Analysis of Results

The buffer pH was **4.73** before adding acid.

The pH changed to **4.69** (0.04 pH units) after addition of 0.010 mols HCl to 1 L of buffer.

a **9.6%** change in acidity

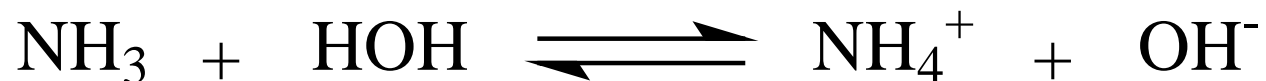
If we added 0.010 mols HCl to 1 L water the pH would fall from **7.00** (the pH of water) to **2.00** (0.010 mols/1 L = 1.00×10^{-2} M)

a **10,000,000%** change in acidity

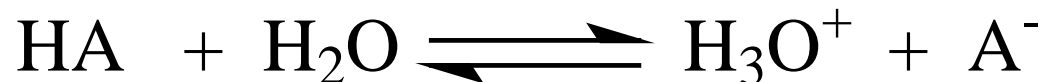
Try One

Q5

For the $\text{NH}_3/\text{NH}_4^+$ buffer problem, calculate the pH after 0.0100 mols HCl are added to 1.00 L of buffer solution.



Henderson Hasselbach Equation



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

log of both sides

$$\log K_a = \log[\text{H}_3\text{O}^+] + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

multiply by (-1)

$$-\log K_a = -\log[\text{H}_3\text{O}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{p}K_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

An Example

Calculate the pH of a solution that is 0.100M in HOCN and 0.150M in NaOCN, using the H/H equation. K_a for HOCN is 3.50×10^{-4}

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\begin{aligned} \text{p}K_a &= -\log K_a \\ &= -\log(3.50 \times 10^{-4}) \\ &= 3.456 \end{aligned}$$

Try One

Q6

Calculate the pH of a solution that is 0.250M in HAc and 0.150M in NaAc, using the H-H equation. K_a for HAc is 1.85×10^{-5} .

Slightly Soluble Salts

Compounds said to be "insoluble" in Chem 1 are really equilibria involving slightly soluble ionic compounds.



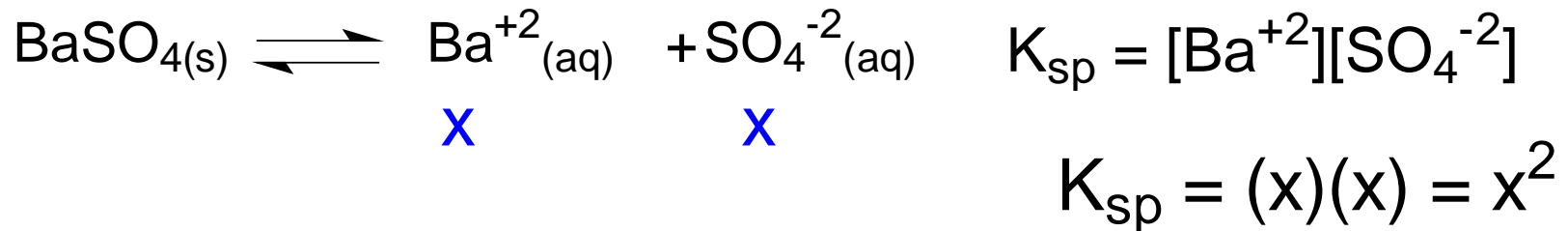
$$K_{sp} = [\text{Ba}^{+2}][\text{SO}_4^{-2}]$$

A Problem to Illustrate

Calculate the molar solubility of barium sulfate.

$$K_{sp} = 1.1 \times 10^{-10}$$

let x = molar solubility of BaSO_4



Another Example

let x = molar solubility of Ag_2CrO_4



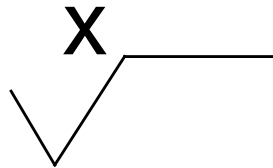
$$K_{\text{sp}} = [\text{Ag}^{+1}]^2 [\text{CrO}_4^{-2}]$$

$2x$ x

Useful Calculator Buttons

$$y^x \quad \text{or} \quad x^y$$

raise any number to any power



takes the "xth" root of a number

Try One

Q7

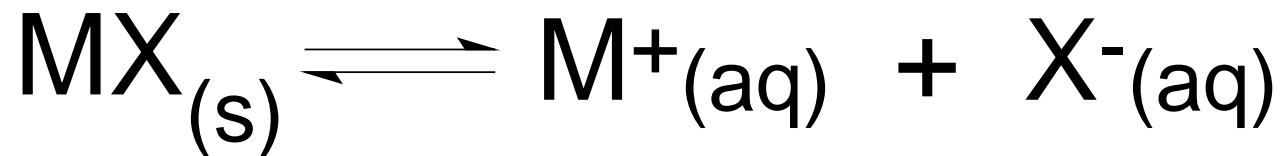
The molar solubility of Ag_2CO_3 is $1.27 \times 10^{-4} \text{M}$.
Calculate K_{sp} for this salt.

Solubility and Common Ions

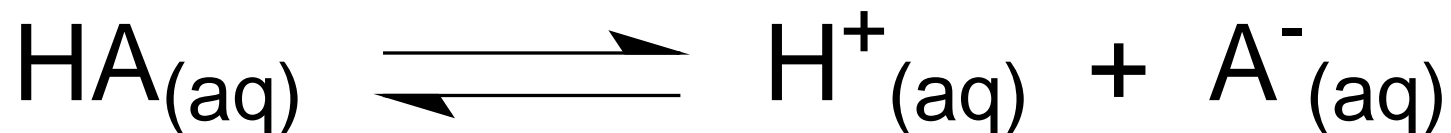
"Ionic compounds are less soluble in a solution that contains a common ion."

based on

LeChatelier's Principle



Buffer Solutions are an Example of the Common Ion Effect



The pH of a 0.10M HAc solution is **2.87**

The pH of a 0.10M HAc solution in 0.010M NaAc is **4.73**

Solubility Examples

Calculate the molar solubility of AgBr in water.



$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = 3.3 \times 10^{-13}$$

let x = the molar solubility of AgBr

Recalculate in 0.15M NaBr

$K_{sp} = [Ag^+] [Br^-] = 3.3 \times 10^{-13}$ let $x =$ the molar solubility of AgBr

$$3.3 \times 10^{-13} = (x)(x + 0.15)$$

$$3.3 \times 10^{-13} = (x)(0.15)$$

This value is **260,000** times less soluble
than in pure water

Try One

Q8

Calculate the molar solubility of MgF_2 in 0.0100M NaF .

K_{sp} for MgF_2 is 6.40×10^{-9} .

Fractional Precipitation

Adding a precipitating reagent to a solution with more than one ion that could form insoluble compounds

A solution is $1.0 \times 10^{-3} \text{M}$ in Cl^- and in Br^- .
Solid AgNO_3 is added gradually.
Would AgBr or AgCl precipitate first?

$$K_{\text{sp}}(\text{AgBr}) = 3.3 \times 10^{-13}$$

$$K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$$

Solution

We solve for the maximum silver ion concentration just before precipitation occurs.

$$K_{sp}(\text{AgBr}) = [\text{Ag}^+] [\text{Br}^-]$$

$$3.3 \times 10^{-13} = [\text{Ag}^+] (1.0 \times 10^{-3})$$

$$[\text{Ag}^+] = 3.3 \times 10^{-10} \text{M}$$

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

$$1.8 \times 10^{-10} = [\text{Ag}^+] (1.0 \times 10^{-3})$$

$$[\text{Ag}^+] = 1.8 \times 10^{-7} \text{M}$$

Another Question

When AgCl starts to precipitate,
what concentration of Br⁻ is left in solution?

**From the previous slide, the [Ag⁺]
to initiate precipitation of AgCl
must be >1.8x10⁻⁷ M**

$$K_{sp}(\text{AgBr}) = [\text{Ag}^+] [\text{Br}^-]$$

$$3.3 \times 10^{-13} = (1.8 \times 10^{-7}) [\text{Br}^-]$$

$$[\text{Br}^-] = 1.8 \times 10^{-6} \text{ M}$$

Try One

Q9

A solution is 0.15M in Pb^{+2} and 0.15M in Ag^{+1} . If SO_4^{-2} ions are slowly added, which would precipitate first, PbSO_4 or Ag_2SO_4 ?

K_{sp} for PbSO_4 is 1.8×10^{-8} and for Ag_2SO_4 is 1.7×10^{-5} .

What is the $[\text{Pb}^{+2}]$ when Ag_2SO_4 begins to precipitate?

Solubility and pH

Calculate the pH of a saturated solution of $\text{Mg}(\text{OH})_2$.

$$K_{\text{sp}} = 1.81 \times 10^{-11}$$



let $x =$ molar sol.

x

2x

$$K_{\text{sp}} = [\text{Mg}^{+2}][\text{OH}^{-1}]^2$$

$$1.81 \times 10^{-11} = (x)(2x)^2 = 4x^3$$

$$x = 1.65 \times 10^{-4} \text{M}$$

Precipitation and pH

At elevated pH, metal ions can precipitate as insoluble hydroxides

At what pH will a 0.10M $\text{Ca}(\text{NO}_3)_2$ solution begin to precipitate $\text{Ca}(\text{OH})_2$?



$$7.9 \times 10^{-6} = K_{sp} = [\text{Ca}^{+2}] [\text{OH}^{-1}]^2$$

Try One

Q10

At what pH will a 0.25M solution of MgCl_2 begin to precipitate $\text{Mg}(\text{OH})_2$?

$$K_{\text{sp}} = 1.5 \times 10^{-11}$$

One Final Note

Be careful with very, very small K's in aqueous media.

Recall that water self ionizes and in "neutral" water $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7} \text{ M}$

In all charts and tables where you said the starting amount of H_3O^+ is "0" it is actually $1.00 \times 10^{-7} \text{ M}$ (same for OH^-)