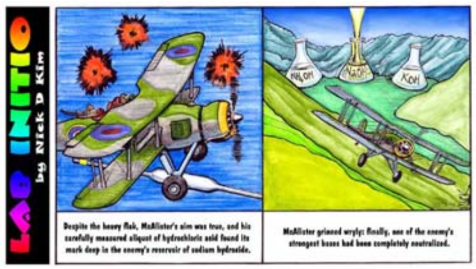
Chemistry BC2001x: General Chemistry I

Lecture 17: Thursday November 12, 2009
Topics: Coupled equilibria
application: the Effect of pH on Solubility
(differs from what is listed on syllabus)

Hand in Problem Set 8

Pick up Set 9



Coupled equilibria

Please note:

- Your textbook does not cover this topic in a systematic way.
- So that you may have detailed notes for future study, a lot of this lecture is on these Powerpoint Slides.
- I strongly recommend that you go to the course web page and print these slides for your notes.

Important Equilibrium Constants

All species are (aq) unless noted otherwise.

K_{eq}	reaction
K_{sp}	salt(s) ⇄ ions
K_a	$HA + H_2O \rightleftarrows H_3O^+ + A^-$
K_b	$B + H_2O \rightleftarrows BH^+ + OH^-$
K_w	$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$

K_a, K_b, K_w: all hydrolysis, reactions with water.
Recall that $K_a(HA)\,K_b(A^-) = K_w$

Numerical values for the above K's for many substances are available from many sources.

Equilibrium Constants
what these numbers mean

The concentrations that appear in any expression for K are the equilibrium values, not the initial ones.

If K >> 1, the reaction as written is strongly favored: lots of product present at equilibrium.

If K << 1, the reaction is not favored: very little will product present at equilibrium.

For insoluble salts K_{sp} values are << 1: these salts dissolve only slightly.

For weak acids and bases K_a and K_b are both << 1: these are only slightly hydrolyzed.

For the reverse reaction:
$H^+ + A^- \rightarrow HA$ $\quad K = 1/K_a \quad K >> 1$
this reaction strongly favors products: goes ~ 100%.
Note that this is NOT K_b: the partner here is H^+ not H_2O.

Review: Combining stepwise K_a values (K_{a1}, K_{a2}) for a diprotic acid

$H_2A \rightleftarrows H^+ + HA^-$

$K_{eq} = K_a(H_2A) = K_{a1}(H_2A) = [H^+][HA^-]/[H_2A]$

$HA^- \rightleftarrows H^+ + A^{2-}$

$K_{eq} = K_a(HA^-) = K_{a2}(H_2A) = [H^+][A^{2-}]/[HA^-]$

the net reaction is $H_2A \rightleftarrows 2\,H^+ + A^{2-}$

$K_{eq} = [H^+]^2[A^{2-}]/[H_2A] = K_{a1}\,K_{a2} = K_{overall}$

The result is general:

the equilibrium constant for the sum of two reactions is the product of their K's.

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COUPLED EQUILIBRIA
Combining equilibrium constants

$A + B \rightarrow C + D$ $\quad K_1 = [C][D]/[A][B]$

$C + E \rightarrow F$ $\quad K_2 = [F]/[C][E]$

These separate equilibria are coupled by the common reagent C, so [F] is related to [A] etc.

We can add the reactions to see this:

$A + B + E \rightarrow D + F$ $\quad K_3 = [D][F]/[A][B][E]$

Observe that $K_3 = K_1K_2$.

At equilibrium, the concentrations satisfy all three K's, so we can use any of them to relate [ ]'s.

If we want to relate [F] to [A] or [B], use K_3

If we want to find [C] use K_1 or K_2.

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This week in lab: Anion Tests
ET-5, ET-6, ET-7
(cations Ag^+, and Ca^{2+} and Ba^{2+})
Solubility of salts in water and acid

1) Will precipitate form between anion and the cation in the test reagent?

2) If so, will it dissolve in strong acid?

Can we predict? Yes: need to look at K_{eq} values for the coupled reactions involving salts and acid.

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SELECTED EQUILIBRIUM CONSTANTS

SALT	K_{sp}	ACID	K_a	aka
$BaSO_3$	8.0×10^{-7}	H_2SO_3	1.2×10^{-2}	$K_{a1}(H_2SO_3)$
Ag_2SO_3	1.5×10^{-14}	HSO_3^-	6.2×10^{-8}	$K_{a2}(H_2SO_3)$
CuS	8.7×10^{-36}	H_2S	1×10^{-7}	$K_{a1}(H_2S)$
$BaSO_4$	1.1×10^{-10}	HS^-	1×10^{-14}	$K_{a2}(H_2S)$
$CaSO_4$	2.4×10^{-5}	HSO_4^-	1.2×10^{-2}	$K_{a2}(H_2SO_4)$
CaF_2	3.9×10^{-11}	HF	7.2×10^{-4}	
$Ca_3(PO_4)_2$	1.2×10^{-32}	CH_3COOH	1.76×10^{-5}	
$Al(OH)_3$	1.9×10^{-33}	H_3PO_4	7.5×10^{-3}	$K_{a1}(H_3PO_4)$
		$H_2PO_4^-$	6.2×10^{-8}	$K_{a2}(H_3PO_4)$
		HPO_4^{2-}	4.2×10^{-13}	$K_{a3}(H_3PO_4)$
		H_2O	1.0×10^{-14}	K_w

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Will the insoluble solid $BaSO_3$ (K_{sp}= 8.0 x 10^{-7}) dissolve in strong acid?

We would like to know the value of K for the reaction:

$$BaSO_3(s) + 2\,H^+(aq) \rightleftarrows Ba^{2+}(aq) + H_2SO_3(aq)$$

If K >> 1, the salt will dissolve.

This is competition for SO_3^{2-} between Ba^{2+} and H^+:

$BaSO_3(s) \rightleftarrows Ba^{2+}(aq) + SO_3^{2-}(aq)$ K = K_{sp}
$2\,H^+(aq) + SO_3^{2-}(aq) \rightleftarrows H_2SO_3(aq)$ K = $1/(K_{a1}K_{a2})$

The *sum* of these two reactions is the overall reaction for dissolving $BaSO_3(s)$ in strong acid.

The equilibrium constant for the net reaction is the *product* of the two K's above.

Will the insoluble solid $BaSO_3$ (K_{sp}= 8.0 x 10^{-7}) dissolve in strong acid?

$$BaSO_3(s) + 2\,H^+(aq) \rightleftarrows Ba^{2+}(aq) + H_2SO_3(aq)$$

Find the value of K_{eq} for the reaction:

$$K = \frac{[Ba^{2+}][H_2SO_3]}{[H^+]^2} \times \frac{[SO_3^{2-}]}{[SO_3^{2-}]}$$

$$= \frac{[H_2SO_3]}{[H^+]^2[SO_3^{2-}]} \times \frac{[Ba^{2+}][SO_3^{2-}]}{1}$$

The insoluble solid $BaSO_3$ (K_{sp}= 8.0 x 10^{-7}) dissolves in strong acid

$$K = \frac{[Ba^{2+}][H_2SO_3]}{[H^+]^2} = \frac{[H_2SO_3]}{[H^+]^2[SO_3^{2-}]} \times \frac{[Ba^{2+}][SO_3^{2-}]}{1}$$

$$= \frac{K_{sp}(BaSO_3)}{K_{a1}(H_2SO_3)K_{a2}(H_2SO_3)} = \frac{(8.0\times10^{-7})}{(1.2\times10^{-2})(6.2\times10^{-8})} = 1.1\times10^{+3}$$

K >> 1: Therefore this salt, $BaSO_3$, which is insoluble in water, dissolves in strong acid.

What about solid Ag_2SO_3 (K_{sp} = 1.5 × 10^{-14}) ?

$$Ag_2SO_3(s) + 2\,H^+(aq) \rightleftarrows 2\,Ag^+(aq) + H_2SO_3(aq)$$

$K_{eq} = K_{sp}(Ag_2SO_3) / K_{a1}(H_2SO_3)\,K_{a2}(H_2SO_3)$
$= 2 \times 10^{-5}$ (K < 1).

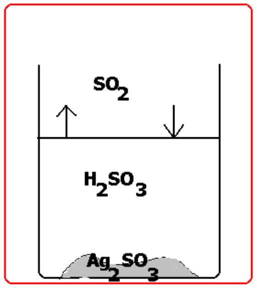
If H_2SO_3 were stable, this would not dissolve.

But Ag_2SO_3 does dissolve in excess strong acid: the small amount of $H_2SO_3(aq)$ formed falls apart, forming $SO_2(g) + H_2O$, removing H_2SO_3 from the reaction mixture.

Following LeChatelier's principle, more acid forms to restore equilibrium, more salt dissolves, and so on, until the salt dissolves completely.
Sulfite salts dissolve in acid (also carbonates).

Solid Ag_2SO_3 $K_{sp} = 1.5 \times 10^{-14}$

If this were carried out in a closed container so the gas couldn't escape, then the process would not go to completion. Formation and escape of $SO_2(g)$ make this reaction proceed 100%.



(Compare to opening a bottle of soda!)

This salt dissolves in acid even though K << 1.

Sulfite precipitates dissolve in strong acids (as do carbonates).

Comparing an insoluble salt with a slightly soluble salt (1)

Will $BaSO_4(s)$ dissolve in strong acid?

$BaSO_4$ is classified as "insoluble" in water. In acid

$$BaSO_4(s) + H^+(aq) \rightleftarrows Ba^{2+}(aq) + HSO_4^-(aq)$$

[does not form H_2SO_4, since that is a *strong* acid.]

$$K = \frac{[Ba^{2+}][HSO_4^-]}{[H^+]} \times \frac{[SO_4^{2-}]}{[SO_4^{2-}]} = \frac{K_{sp}(BaSO_4)}{K_a(HSO_4^-)} = \frac{1.1\times10^{-10}}{1.2\times10^{-2}} = 9.2\times10^{-9} << 1$$

K << 1, so this reaction does not proceed much.
$BaSO_4$ remains insoluble even in strong acid.

Comparing an insoluble salt with a slightly soluble salt (2)

Will $CaSO_4(s)$ dissolve in strong acid?

$CaSO_4$ is classified as "slightly soluble".

$$CaSO_4(s) + H^+(aq) \rightleftarrows Ca^{2+}(aq) + HSO_4^-(aq)$$

$$K = \frac{[Ca^{2+}][HSO_4^-]}{[H^+]} \times \frac{[SO_4^{2-}]}{[SO_4^{2-}]} = \frac{K_{sp}(CaSO_4)}{K_a(HSO_4^-)} = \frac{2.4\times10^{-5}}{1.2\times10^{-2}} = 2.0\times10^{-3} < 1$$

K < 1, but not by a whole lot.

How much $CaSO_4(s)$ will dissolve in a solution with $[H^+] = 1.0$ (pH = 0)?

$$CaSO_4(s) + H^+(aq) \rightleftarrows Ca^{2+}(aq) + HSO_4^-(aq)$$

K = 0.0020 (from previous slide)

Let x = molar solubility of $CaSO_4$ in pH 0

$x = [HSO_4^-] = [Ca^{2+}]$

$K_{eq} = x^2 / (1.00) \rightarrow x = 0.044$ M.

Consider 1 mL of acid solution:
0.044 mmoles $CaSO_4(s)$ can dissolve in it.
Formula weight is 136.14 g/mole

→ 6.1 mg $CaSO_4(s)$ dissolves (not very much).

How much $CaSO_4(s)$ dissolves in an acidic solution with $[H^+]$ = 1.0? (2)

$CaSO_4(s) + H^+(aq) \rightleftarrows Ca^{2+}(aq) + HSO_4^-(aq)$

From previous slide:
Molar solubility in pH=0 solution is 0.044 M.

Compare with the solubility in pure water:

$s = K_{sp}^{1/2}$ = 0.0049 M

$CaSO_4(s)$ dissolves in acid about 10 times more than in water, but still not very much.

Whether it all dissolves depends on amount: a large amount of solid will not dissolve, but a small amount will. Making the acid much more concentrated increases.

General observation: Most sulfide salts do not dissolve even in strong acid. Why not?

$CuS(s) + 2 H^+ \xrightarrow{?} Cu^{2+} + H_2S(aq)$

If enough $H_2S(aq)$ forms, its concentration will exceed the solubility of the gas. Gas will escape,

$H_2S(aq) \rightarrow H_2S(g)$

forcing the first reaction towards products.

If K_{aq} for the first reaction is very small, then $[H_2S(aq)]$ will be so small that no $H_2S(g)$ escapes

So: will CuS dissolve in strong acid?

$K_{sp}(CuS) = 8.7 \times 10^{-36}$ CuS is very insoluble!

H_2S is a very weak acid: $K_{a1}K_{a2} = 1.0 \times 10^{-21}$

General observation: Most sulfide salts will not dissolve even in strong acid.

Calculate K_{eq} for the dissolution reaction

$CuS(s) + 2 H^+(aq) \rightleftarrows Cu^{2+}(aq) + H_2S(aq)$

assuming that the H_2S stays in solution:

$$K = \frac{[Cu^{2+}][H_2S]}{[H^+]^2} \times \frac{[S^{2-}]}{[S^{2-}]}$$

$$= \frac{[Cu^{2+}][S^{2-}]}{1} \frac{[H_2S]}{[H^+]^2[S^{2-}]} = \frac{K_{sp}(CuS)}{K_{a1}(H_2S)K_{a2}(H_2S)} = 8.7 \times 10^{-15} << 1$$

VERY SMALL. Most sulfides are NOT soluble even in strong acid; the values of K_{sp} are simply too small.

What is $[H_2S]$ in a saturated solution of CuS(s) at a pH of 1.0?

$CuS(s) + 2 H^+(aq) \rightleftarrows Cu^{2+}(aq) + H_2S(aq)$

Let x= the molar solubility of CuS(s) in this strongly acidic solution. At this pH, the S^{2-} will be essentially completely converted to H_2S.

Then $[Cu^{2+}] = [H_2S] = x$

and $K = x^2/(0.10)^2 = 8.7 \times 10^{-15}$

so $x = 9 \times 10^{-7}$ M.

This very tiny concentration is below saturation. Thus no gas escapes: no bubbles are seen and no rotten egg odor.

The difference between strong and weak acids in dissolving insoluble salts.

Consider $BaF_2(s)$: $K_{sp} = 1.7 \times 10^{-6}$
Does it dissolve in strong acid?

$$BaF_2(s) + 2\ H^+ \rightleftarrows Ba^{2+} + 2\ HF$$

Ba^{2+} and H^+ compete for F^-

$K_{eq} = [Ba^{2+}][HF]^2/[H^+]^2 \times [F^-]^2/[F^-]^2$

$= [Ba^{2+}][F^-]^2 \times [HF]^2/[H^+]^2[F^-]^2$

$= K_{sp}(BaF_2)/K_a(HF)^2$

$= (1.7 \times 10^{-6})/(7.2 \times 10^{-4})^2 = 3.2$

Yes, quite a bit dissolves: K > 1.

The difference between strong and weak acids in dissolving insoluble salts.

Consider $BaF_2(s)$: $K_{sp} = 1.7 \times 10^{-6}$

Does it dissolve in weak acid HOAc?

$$BaF_2(s) + 2\ HOAc \rightleftarrows Ba^{2+} + 2\ HF + 2\ OAc^-$$

$K_{eq} = [Ba^{2+}][HF]^2[OAc^-]^2/[HOAc]^2$

$\times [F^-]^2/[F^-]^2 \times [H^+]^2/[H^+]^2$

$K_{eq} = \{[Ba^{2+}][F^-]^2\}\ \{[H^+]^2[OAc^-]^2/[HOAc]^2\}\ \{[HF]^2/[H^+]^2[F^-]^2\}$

$= K_{sp}(BaF_2)\ K_a(HOAc)^2\ /\ K_a(HF)^2$

$= (1.7 \times 10^{-6})(1.8 \times 10^{-5})^2\ /\ (7.2 \times 10^{-4})^2$

$= 1.1 \times 10^{-9}$ Very little dissolves: K << 1.

The difference between strong and weak acids in dissolving insoluble salts.

Conclusion: $BaF_2(s)$ dissolves in strong acid, but not in weak (HOAc).

$CaF_2(s)$, with a smaller K_{sp} (3.9×10^{-11}), dissolves only a little in strong acid, and much less in weak acid (HOAc).

In ET-6 you will observe that CaF_2 precipitate forms when Ca^{2+} ion is added to a solution of F^- ion in the presence of acetic acid.

This is equivalent to saying that $CaF_2(s)$ would not dissolve in acetic acid.

Dissolution of $Ca_3(PO_4)_2$ ($K_{sp} = 1.2 \times 10^{-32}$) in (weak) acetic acid?

$$Ca_3(PO_4)_2(s) + 4\ HOAc \rightleftarrows 3\ Ca^{2+} + 2\ H_2PO_4^- + 4\ OAc^-$$

Competition between Ca^{2+} and H^+ for PO_4^{3-}, and between OAc^- and PO_4^{3-} for H^+.

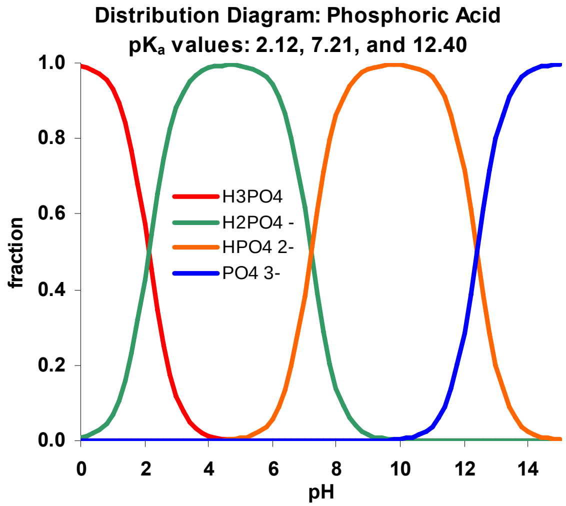
Note: protonation of is PO_4^{3-} *not* complete here. H_3PO_4 is the major form only when pH is less than ~2, since $pK_{a1}(H_3PO_4) = 2.12$.

(See the following distribution diagram)

Even *concentrated* acetic acid is not that acidic.

This is why you are instructed to write $H_2PO_4^-$ in your balanced equations.

At pH values between ~2 and ~7, $H_2PO_4^-$ is the dominant species



Dissolution of $Ca_3(PO_4)_2$ in acetic acid?

$Ca_3(PO_4)_2(s) + 4\ HOAc \rightleftarrows 3\ Ca^{2+} + 2\ H_2PO_4^- + 4\ OAc^-$

$$K = \frac{[Ca^{2+}]^3[H_2PO_4^-]^2[OAc^-]^4}{[HOAc]^4} \times \frac{[PO_4^{3-}]^2}{[PO_4^{3-}]^2} \times \frac{[H^+]^4}{[H^+]^4}$$

$$= \frac{K_{sp}(Ca_3(PO_4)_2)\{[K_a(HOAc)\}^4}{\{K_{a2}(H_3PO_4)\}^2\{K_{a3}(H_3PO_4)\}^2} = \frac{(1.2\times10^{-29})\times(1.76\times10^{-5})^4}{(6.2\times10^{-8})^2\times(4.2\times10^{-13})^2}$$

$$= 1.7\times10^{-9} << 1$$

The reaction does not proceed to a great extent. This insoluble phosphate does not dissolve much in weak acid. Let's see how much will dissolve...

$Ca_3(PO_4)_2(s) + 4\ HOAc \rightleftarrows 3\ Ca^{2+} + 2\ H_2PO_4^- + 4\ OAc^-$
$K = 1.7 \times 10^{-9}$

Would 0.04 moles/L salt dissolve in 6.0 M HOAc?

Then $[Ca^{2+}] = 0.12$ M, $[H_2PO_4^-] = 0.08$ M, $[OAc^-] = 0.16$ M, and $[HOAc] = 6.0 - 0.16 = 5.84$ M.

The reaction quotient Q has the value

$Q = (0.12)^3(0.08)^2(0.16)^4/(5.8)^4 = 6.2 \times 10^{-12} << K$

So 0.040 moles solid calcium phosphate will dissolve in 1 L concentrated (6 M) acetic acid, even though the salt is very insoluble in water and the acid is weak.

Would 0.10 moles/L dissolve in 6.0 M HOAc?

$[Ca^{2+}] = 0.3$ M, $[H_2PO_4^-] = 0.2$ M, $[OAc^-] = 0.4$ M, and $[HOAc] = 5.6$ M. $Q = 2.8 \times 10^{-8} > K$ No.

The molar solubility s is $0.04 < s < 0.10$ M.

$Ca_3(PO_4)_2(s) + 4\ HOAc \rightleftarrows 3\ Ca^{2+} + 2\ H_2PO_4^- + 4\ OAc^-$
$K = 1.7 \times 10^{-9}$

Calculate the exact molar solubility:

Let s = moles/L salt that will dissolve in 6 M HOAc.

$[Ca^{2+}] = 3s$, $[H_2PO_4^-] = 2s$, $[OAc^-] = 4s$,

approx: $[HOAc] = (6.0-4s) \approx 6.0$ (since $s < 0.1$)

$K = (3s)^3(2s)^2(4s)^4/(6.0)^4 = 27648\ s^9 / 1296$

$= 21.33\ s^9 = 1.7 \times 10^{-9} \rightarrow$

$s = [(1.7 \times 10^{-9})/21.33]^{1/9}$

= 0.075 moles/L $Ca_3(PO_4)_2(s)$ will dissolve.

Check: 4(0.075) = 0.3: less than 10% of 6.0. ok

(Successive approximations give s = 0.074 M.)

Quite a bit dissolves, even with small K.