

CHEM 206 section 01

LECTURE #26

Fri. April 11, 2008

LECTURE TOPICS:

TODAY'S CLASS: finish Ch.18 to 18.5

FINAL EXAM: Saturday April 19th (9am-12pm)

▪ **Covers entire course:** Ch.6, 9.8, 19, 13.1-5,
14, 15, 16, 17, 18.1-5

FINAL EXAMS FROM PREVIOUS YEARS ON WEBSITE

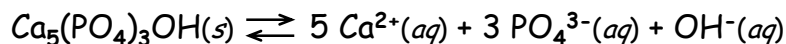
Moodle site has link to: <http://faculty.concordia.ca/rogers>

(1)

18.4 Solubility of salts - *more Applied Equilibria!*

CLASSIC EXAMPLE: Tooth enamel

- contains insoluble mineral, hydroxyapatite: $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
- in constant contact with water:



SO WHY DOES TOOTH DECAY OCCUR?

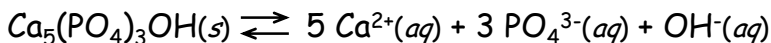
Even if only a small amount dissolves:

- OH^{-} ions are released
- react with acids in foods
& acids produced by bacteria in plaque
- equilibrium shifts right!
⇒ tooth decay occurs when mouth is acidic!

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Another "special" eqm constant: Solubility Product, K_{sp}

In an aqueous solution **saturated** with an ionic compound:
equal rates of dissolving & precipitating...



$$K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-] = 6.8 \times 10^{-37}$$

= "solubility product"

hydroxyapatite
is highly insoluble

⇒ Very small K_{sp}
⇒ but trace amount
will dissolve if left
in contact with water

Heterogeneous eqm involving undissolved solid

- pure solid's conc. is constant...
- not actually "ignored" in eqm expression

If solution not saturated, not at eqm:

$$Q_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-] = ???$$

= "ion product"

(3) K_{sp} magnitude includes **both** solubility & salt's ion ratio
⇒ be careful estimating relative solubilities based on K_{sp}

Relative terms: Soluble, slightly soluble & insoluble...

SOLUBLE SALTS: Large K_{sp} ⇒ high solubility ("sol'y")
= high [ions] in sat'd sol'n

Salts with $K_{sp} > 1$ not listed in tables:
alkali metal salts, nitrate salts, most halide salts...
remember solubility trends from Chem 205 - Kotz Ch.5

SLIGHTLY SOLUBLE SALTS: Moderate K_{sp}

- Ag₂SO₄ $K_{sp} = 1.2 \times 10^{-5}$
- PbCl₂ $K_{sp} = 1.6 \times 10^{-5}$

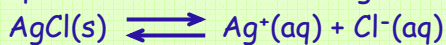
INSOLUBLE SALTS: Very small K_{sp} ⇒ very low sol'y

Trace amounts will dissolve:

- AgCl $K_{sp} = 1.8 \times 10^{-10}$ "Ag halides are insoluble..."
- Ca₃(PO₄)₂ $K_{sp} = 1.3 \times 10^{-32}$ BONE!
- Fe(OH)₃ $K_{sp} = 4 \times 10^{-38}$ a component of rust...
- HgS $K_{sp} = 1.6 \times 10^{-54}$ insoluble red mineral *cinnabar*

Note: K_{sp} value includes **solubility AND ions/formula unit** info.

At 25°C, the eqm constant for dissolving solid AgCl is 1.8×10^{-10} :



Calculate the free E for precipitating AgCl(s) under std conditions.

$$K = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] \quad \text{AgCl}(s) \text{ not included because it is a SOLID...}$$

$$\begin{aligned} K \text{ for precipitation} &= \text{reciprocal of } K \text{ for dissolving} \\ &= 1/(1.8 \times 10^{-10}) \\ &= 5.6 \times 10^9 \quad \dots \text{a } K_c \text{ since reactants in solution} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= -RT \ln K \\ &= -(8.324 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1})(298\text{K}) \ln(5.6 \times 10^9) \\ &= -556100 \text{ J}\cdot\text{mol}^{-1} = -560 \text{ kJ}\cdot\text{mol}^{-1} \text{ to 2 SF} \end{aligned}$$

→ this came from a K_c thus applies to reactants in solution at std conditions: $[] = 1 \text{ M}$, $T = 298 \text{ K}$

$\Delta G^\circ < 0 \Rightarrow$ pptn of AgCl(s) is thermodynamically favoured!
Spontaneous fwd rxn \Rightarrow product-favoured \Rightarrow it's not very soluble!

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Solubility & Concentration of dissolved ions

SOLUBILITY of a substance: "s"

= maximum amount of substance that will dissolve (in water) at a given temperature (usually expressed as g/100mL at 25°C)

s = concentration of a SATURATED SOLUTION

recall: to prepare a saturated solution, keep adding solute until some remains UNDISSOLVED

In sat'd sol'n: **rate of dissolution = rate of precipitation**
 \Rightarrow *i.e.*, a saturated solution is at EQM!

Is "solubility" the same as "dissolved ion concentration"?
Sometimes yes, sometimes no:



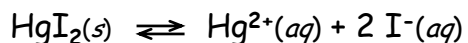
"Solubility" = **s** = amount of compound dissolved in given volume,

$$\text{Here: } s = [\text{Bi}_2\text{S}_3] = \frac{1}{2}[\text{Bi}^{3+}] = \frac{1}{3}[\text{S}^{2-}]$$

Remember: solubility depends on what else is present in the soln...
e.g., a common ion? or something that reacts with the ion(s)?

Ex.1: Determining ion concentrations (sat'd sol'ns) using K_{sp}

You are working with mercuric iodide, HgI_2 ($K_{sp} = 3 \times 10^{-29}$). What will the concentrations of each ion be in a saturated aqueous solution at room temperature?



Initial	present	0	0 M
Change		+x	+2x
Eqm	present	x	2x

Notice impact of 1:2 ion ratio
 $K_{sp} = [\text{Hg}^{2+}][\text{I}^{-}]^2$

Note: Let $[\text{HgI}_2]$ dissolved = x = same as solubility, s !
 (can use ICE table, but don't need to...)

$$\begin{aligned} K_{sp} &= [\text{Hg}^{2+}][\text{I}^{-}]^2 \\ 3 \times 10^{-29} &= (x)(2x)^2 \\ &= 4x^3 \\ x &= 2 \times 10^{-10} \text{ M} \end{aligned}$$

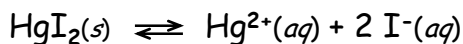
$$\begin{aligned} \Rightarrow [\text{Hg}^{2+}] &= 2 \times 10^{-10} \text{ M} \\ [\text{I}^{-}] &= 4 \times 10^{-10} \text{ M} \end{aligned}$$

In a saturated solution of HgI_2 (ie., solution in eqm with solid!)

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Ex.2: Effect of common ion on solubility - v.1

How different is the solubility of HgI_2 ($K_{sp} = 3 \times 10^{-29}$) in water vs. in 0.050 NaI sol'n? Last ex - in water: $[\text{Hg}^{2+}]_{\text{sat'd}} = 2 \times 10^{-10} \text{ M}$



Initial	present	0	0.050 M
Change		+x	+2x
Eqm	present	x	0.050 + 2x

$$K_{sp} = [\text{Hg}^{2+}][\text{I}^{-}]^2$$

Some I^{-} already present in solution, so:

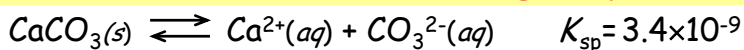
$$3 \times 10^{-29} = (x)(0.050 + 2x)^2 \quad \text{Note small } K_{sp} \dots \text{use approx'n:}$$

$$3 \times 10^{-29} \approx (x)(0.050)^2$$

$$x = 1 \times 10^{-26} = [\text{Hg}^{2+}] = [\text{HgI}_2]_{\text{max}} \text{ in 0.050M NaI solution}$$

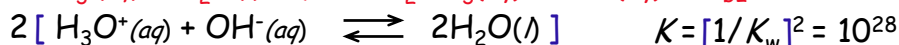
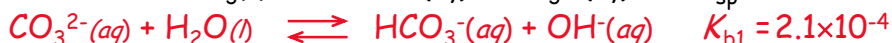
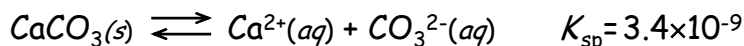
- 1.) Solubility decreases in presence of common ion
- 2.) Solubility increases if common ion is removed via rxn (e.g., if ion is basic & we make the solution acidic...)

Common ion effect - v.2: reacting away an ion (pH effect)



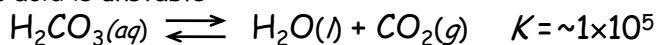
Basic anion \Rightarrow eqm will shift right in acid!

Ex.3: Limestone dissolves in acid & bubbles of gas form. WHY?



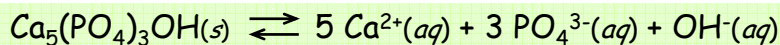
When add rxns eqns \Rightarrow multiply Ks: $K_{net} = K_{sp}K_{b1}K_{b2}K = 1.7 \times 10^8$

But recall: carbonic acid is unstable:



Large $K \Rightarrow$ fully soluble in acid, + gaseous product. $K_{overall} = 2 \times 10^{13}$!
 (...& gas leaves... \therefore might never reach eqm, just keeps shifting right...)

Things we can do with solubility equilibria



$$K_{sp} = [\text{Ca}^{2+}]^5[\text{PO}_4^{3-}]^3[\text{OH}^-] = 6.8 \times 10^{-37}$$

Highly soluble in acid (due to consumption of OH^-)

Highly insoluble in base (due to common ion effect)

Product of dissolved ion concentrations is CONSTANT...

- Can calculate **conc. of ions in a sat'd sol'n** of any ionic compound whose K_{sp} is known
- If have another source of "**common**" ion, the solid won't be as soluble as in pure water...
- If one of the ions is **consumed via another reaction**, the solid will be more soluble than in pure water...
- Can determine whether a given mixture will exceed max. solubility of dissolved solids \Rightarrow **will ppt form ($Q_{sp} > K_{sp}$)?**

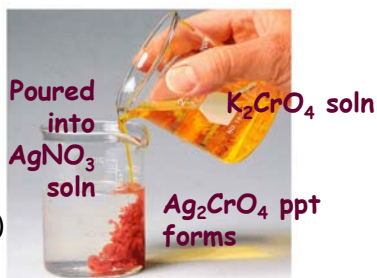
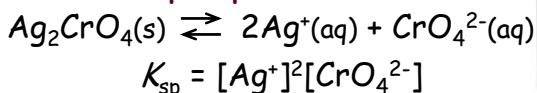
18.5 Precipitation reactions (last 206 text section)

- Solubility differences are used to separate ions *(details? 15.7)*
- Can determine if a precipitate will form when solutions are mixed...or when add solid to a soln...etc.
(you ARE responsible for this -- simple application of Q vs. K !)

Initially: Reaction quotient (Q) = Ion product, Q_{sp}
 At eqm: Equilibrium constant (K) = Solubility product, K_{sp}

WHEN YOU HAVE DONE PRECIPITATIONS IN THE LAB \Rightarrow

SOMEONE DID THE MATH 1st...
 to be sure that $Q_{sp} > K_{sp}$
 (too many ions compared to eqm...)
 so that precipitation would occur!!



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Ex. 4: Will this person get kidney stones? W05 final, #10

People develop kidney stones when insoluble compounds like calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ ($K_{sp} \approx 1 \times 10^{-25}$) precipitate out of their urine.

Urine normally contains about 5.33 g/L of Ca^{2+} ions. What concentration of phosphate ions (in molarity) would cause calcium phosphate to begin precipitating from urine?



In urine (*fixed*): $[\text{Ca}^{2+}]_o = \frac{(5.33 \text{ g} / 40.08 \text{ g/mol})}{1 \text{ L}} = 0.1330 \text{ mol/L}$

Precipitation will occur as soon as: $Q_{sp} > K_{sp}$ \leftarrow let's find $[\text{PO}_4^{3-}]$ needed for $Q = K$

$$Q_{sp} = K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

$$1 \times 10^{-25} = (0.1330 \text{ M})^3 [\text{PO}_4^{3-}]^2$$

$$\Rightarrow [\text{PO}_4^{3-}] = \sqrt{(1 \times 10^{-25} / (0.1330 \text{ M})^3)}$$

$$\approx 7 \times 10^{-12} \text{ M} \quad \leftarrow \text{above this } [\text{PO}_4^{3-}], \text{Ca}_3(\text{PO}_4)_2(s) \text{ precipitation would occur}$$

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Ex.5: Waste-water treatment & toxic waste

Allowed limit in waste-water: $[Pb^{2+}] < 5 \text{ ppm } (\approx \text{mg/L})$
 Higher than this conc.: must treat as "toxic waste"
 disposal is expensive!
 To $\downarrow [Pb^{2+}]$: add something to ppt lead as insoluble salt

APPROACH:

- add precipitating agent (cheap, non-toxic...)
- filter off ppt & dispose of with toxic waste
- measure $[Pb^{2+}]$ remaining in solution (= $[Pb^{2+}]_{eqm}$...)
- If $[Pb^{2+}]_{eqm} < 5 \text{ mg/L}$, dispose of with regular waste...

1 possibility:

NaCl
 ppt out $PbX_2(s)$



Note: must convert ppm to molarity to use eqm expression...

$$\left(\frac{5 \text{ mg } Pb^{2+}}{1 \text{ kg soln}} \right) \times \left(\frac{1 \text{ kg soln}}{1 \text{ L soln}} \right) \times \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \times \left(\frac{1 \text{ mol } Pb^{2+}}{207.2 \text{ g}} \right) = 2.41 \times 10^{-5} \text{ M}$$

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NaCl is CHEAP! & $PbCl_2$ only slightly soluble, $K_{sp} = 1.6 \times 10^{-5}$.
 How much NaCl must be added to 500 L of a waste solution containing 10 mg/L dissolved lead in order to decrease the dissolved lead to 5 mg/L ($2.41 \times 10^{-5} \text{ M}$)?



I.	<i>present</i>	$4.83 \times 10^{-5} \text{ M}$	<i>Initial = $[Cl^{-}]_0$</i>
C.	$+x$	$-x = -2.41 \times 10^{-5}$	$-2x = -4.83 \times 10^{-5}$
E.	<i>less...</i>	$2.41 \times 10^{-5} \text{ M}$	<i>Eqm = $[Cl^{-}]_{eqm}$</i>

Precipitation leads to eqm being established:

$$1.6 \times 10^{-5} = (2.41 \times 10^{-5}) ([Cl^{-}]_{eqm})^2$$

$$([Cl^{-}]_{eqm})^2 = 0.6639$$

$$[Cl^{-}]_{eqm} = 0.8148 \text{ M}$$

So: $[Cl^{-}]_{initial} = [Cl^{-}]_{eqm} + 4.83 \times 10^{-5} \text{ M}$
 $= 0.8148 + 4.83 \times 10^{-5} \text{ M}$
 $\approx 0.8148 \text{ M}$

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To treat 500 L wastewater:

$$n_{NaCl} = (500 \text{ L})(0.8148 \text{ M})$$

$$= 407 \text{ mol NaCl required}$$

$$m_{NaCl} = 407 \text{ mol} \times 58.45 \text{ g/mol}$$

$$= 23800 \text{ g}$$

$$\approx 24 \text{ kg (to 1 SF = 20 kg)}$$

But, add MORE to be certain...

FINAL EXAM INFORMATION

- **Final exam: Saturday April 19th (9am-12pm)**
- **Covers entire course: Ch.6, 9.8, 19, 13.1-5, 14, 15, 16, 17, 18.1-5**
- The examination room invigilators are VERY STRICT:
 - Student ID card mandatory
 - No programmable calculators
 - **No electronic dictionaries, cell phones, pagers, blackberries, etc**
 - Book-format translation dictionaries (word-to-word only) allowed, but they will be inspected.
 - Arrive to the exam room early !

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Sample exam question

Winter 2004 section 02

7. (/ 9 marks) You are asked to prepare a 100.0 mL sample of a solution with pH of 5.50 by dissolving the appropriate amount of a solute in pure water (pH 7.00). Which ONE of the following solutes would you use, and in what quantity? EXPLAIN YOUR CHOICE, AND SHOW ALL RELEVANT CALCULATIONS.

CIRCLE YOUR CHOICE:

- 15 M $\text{NH}_3(\text{aq})$
- 12 M $\text{HCl}(\text{aq})$
- $\text{NH}_4\text{Cl}(\text{s})$
- Pure ("glacial") acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$

SUBSTANCE	K_a
HCl	very large
$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}
NH_4^+	5.6×10^{-10}
H_2O	$K_w = 1 \times 10^{-14}$

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Sample exam question

Winter 2004 section 51

10. (___ / 9 Marks) The ancient Romans added calcium sulfate to wine to clarify it (*i.e.*, to remove cloudiness). They didn't know it at the time, but this treatment also removed any dissolved lead in the wine. [Note: Roman water pipes were made of lead, and wealthy people drank from lead cups....]

- a) What is the maximum concentration of dissolved lead (II) ions, in molarity, that might be present in wine to which excess calcium sulfate has been added? [$K_{sp} \text{PbSO}_4 = 1.6 \times 10^{-8}$; $K_{sp} \text{CaSO}_4 = 6.1 \times 10^{-5}$]

- a) Chronic exposure to lead is dangerous, particularly to children, because lead is a poison that builds up in the bloodstream. Even very low concentrations of lead in the blood (50 parts per billion, = 0.050 ppm) causes increased blood pressure; above 100 ppb, intelligence is affected, and coma or death can result above 800 ppb. **Convert the concentration of Pb^{2+} ions in the wine from part (a) to parts per billion, ppb, and comment on whether or not you think the fall of the Roman Empire might have been related to lead poisoning.**

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Sample exam question

Fall 2004 section 52

10. (___ / 12 Marks) You are working in a biology lab and are asked to prepare a pH 7.40 buffer that mimics human blood. You will use KH_2PO_4 and Na_2HPO_4 . The K_a of H_2PO_4^- is 6.3×10^{-8} ; the K_a of HPO_4^{2-} is 4.2×10^{-13} .

- a) (3 marks) Briefly explain why HPO_4^{2-} and H_2PO_4^- are a good pair of substances to use.

- a) (3 marks) What should be the ratio of $[\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$ in this buffer?

- a) (6 marks) To mimic blood, the buffer must exert an osmotic pressure of $\pi = 8.00$ atm at 37°C . Using this information, calculate the masses of KH_2PO_4 and Na_2HPO_4 you should use to prepare 1.0 L of buffer.

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