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

18.4 Solubility of salts – *more Applied Equilibria!*

CLASSIC EXAMPLE: Tooth enamel

- contains insoluble mineral, hydroxyapatite: $Ca_5(PO_4)_3OH$
- in constant contact with water:

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5\,Ca^{2+}(aq) + 3\,PO_4^{3-}(aq) + OH^-(aq)$$

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!

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

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

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5\ Ca^{2+}(aq) + 3\ PO_4^{3-}(aq) + OH^-(aq)$$

$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-] = 6.8\text{x}10^{-37}$$

= "solubility product"

hydroxyapatite
is highly insoluble
⇨Very small K_{sp}
⇨but <u>trace amount</u>
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:

$$Q_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-] = ???$$

= "ion product"

K_{sp} magnitude includes <u>both</u> 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}

- Ag_2SO_4 $K_{sp} = 1.2\text{x}10^{-5}$
- $PbCl_2$ $K_{sp} = 1.6\text{x}10^{-5}$

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

Trace amounts will dissolve:

- $AgCl$ $K_{sp} = 1.8\text{x}10^{-10}$ "Ag halides are insoluble…"
- $Ca_3(PO_4)_2$ $K_{sp} = 1.3\text{x}10^{-32}$ BONE!
- $Fe(OH)_3$ $K_{sp} = 4\text{x}10^{-38}$ a component of rust…
- HgS $K_{sp} = 1.6\text{x}10^{-54}$ 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}:

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

Calculate the free E for <u>precipitating</u> AgCl(s) under std conditions.

$K = 1.8\times10^{-10} = [Ag^{+}][Cl^{-}]$ AgCl(s) not included because it is a SOLID…

K for precipitation = reciprocal of K for dissolving
$= 1/(1.8\times10^{-10})$
$= 5.6\times10^{9}$ …a K_c since reactants in solution

$\Delta G° = -RT \ln K$
$= -(8.324\ J\cdot mol^{-1}K^{-1})(298K)\ \ln(5.6\times10^{9})$
$= -556100\ J\cdot mol^{-1}$ = *$-560\ kJ\cdot mol^{-1}$ to 2 SF*

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

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

Solubility & Concentration of dissolved ions

<u>SOLUBILITY of a substance</u>: "*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
⇨ *i.e.,* a saturated solution is at EQM !

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

$$Bi_2S_3(s) \rightleftharpoons 2\,Bi^{3+}(aq) + 3\,S^{2-}(aq)$$

"Solubility" = s = amount of <u>compound</u> dissolved in given volume,
Here: $s = [Bi_2S_3] = {}^{1}/_{2}[Bi^{3+}] = {}^{1}/_{3}[S^{2-}]$

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} = 3x10^{-29}).
What will the concentrations of each ion be in a saturated aqueous solution at room temperature?

$$HgI_2(s) \rightleftarrows Hg^{2+}(aq) + 2\,I^-(aq)$$

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

Notice impact of 1:2 ion ratio

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

Note: **Let $[HgI_2]$ dissolved = x = same as solubility, *s* !**
(can use ICE table, but don't need to…)

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

$\Rightarrow [Hg^{2+}] = 2\text{x}10^{-10}$ M
$[I^-] = 4\text{x}10^{-10}$ M

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

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

How different is the solubility of HgI_2 (K_{sp} = 3x10^{-29}) in water *vs.* in 0.050 NaI sol'n? *Last ex - in water: $[Hg^{2+}]_{satd}$ = 2x10^{-10} M*

$$HgI_2(s) \rightleftarrows Hg^{2+}(aq) + 2\,I^-(aq)$$

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

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

Some I^- already present in solution, so:

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

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

$x = 1\text{x}10^{-26} = [Hg^{2+}] = [HgI_2]_{max}$ 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)

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = 3.4\times10^{-9}$

Basic anion ⇨ eqm will shift right in acid!

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

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = 3.4\times10^{-9}$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad K_{b1} = 2.1\times10^{-4}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \qquad K_{b2} = 2.4\times10^{-8}$$

$$2\,[\,H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)\,] \qquad K = [1/K_w]^2 = 10^{28}$$

NET: $CaCO_3(s) + 2H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + H_2CO_3(aq) + 2H_2O(l)$

When add rxns eqns ⇨ multiply *K*s: $K_{net} = K_{sp}K_{b1}K_{b2}K = 1.7\times10^8$

But recall: carbonic acid is unstable:

$$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g) \qquad K = \sim1\times10^5$$

$CaCO_3(s) + 2H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + CO_2(g) + 3H_2O(l)$

Large K ⇨ fully soluble in acid, + gaseous product. $K_{overall} = 2\times10^{13}$!

(…& gas leaves… ∴might never reach eqm, just keeps shifting right…)

Things we can do with solubility equilibria

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5\,Ca^{2+}(aq) + 3\,PO_4^{3-}(aq) + OH^-(aq)$$

$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-] = 6.8\text{x}10^{-37}$$

Highly soluble in acid (due to consumption of OH^-)
Highly <u>in</u>soluble 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 ⇨ 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 <u>this</u> -- 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 ⇨

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

$$Ag_2CrO_4(s) \rightleftarrows 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

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

People develop kidney stones when insoluble compounds like calcium phosphate, $Ca_3(PO_4)_2$ ($K_{sp} \approx 1\times10^{-25}$) 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?

$$Ca_3(PO_4)_2(s) \rightleftarrows 3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq) \qquad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

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

Precipitation will occur as soon as: $Q_{sp} > K_{sp}$ ← let's find $[PO_4^{3-}]$ needed for $Q = K$

$$Q_{sp} = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

$$1\text{x}10^{-25} = (0.1330\ M)^3\ [PO_4^{3-}]^2$$

$$⇨\ [PO_4^{3-}] = \sqrt{(1\text{x}10^{-25}\ /\ (0.1330\ M)^3)}$$

$$\approx\ 7\text{x}10^{-12}\ M$$

← <u>above</u> this $[PO_4^{3-}]$, $Ca_3(PO_4)_2(s)$ precipitation would occur

Ex.5: Waste-water treatment & toxic waste

Allowed limit in waste-water: $[Pb^{2+}] < 5$ ppm (≈ mg/L)
Higher than this conc.: must treat as "toxic waste"
disposal is expensive!
To ↓ $[Pb^{2+}]$: 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 $[Pb^{2+}]_{eqm} < 5$ mg/L, dispose of with regular waste…

1 possibility:
NaCl
ppt out $PbX_2(s)$

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

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

$$\left(\frac{5\ \cancel{mg}\ Pb^{2+}}{1\ \cancel{kg\ soln}}\right) \times \left(\frac{1\ \cancel{kg\ soln}}{1\ L\ soln}\right) \times \left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right) \times \left(\frac{1\ mol\ Pb^{2+}}{207.2\ \cancel{g}}\right) = 2.41\times10^{-5}\ M$$

NaCl is CHEAP! & $PbCl_2$ only slightly soluble, $K_{sp} = 1.6\times10^{-5}$.
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 (2.41×10^{-5} M)?

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = [Pb^{2+}][Cl^-]^2$$

I.	*present*	*4.83×10^{-5} M*	*Initial = $[Cl^-]_o$*
C.	*+ x*	*- x = -2.41×10^{-5}*	*- 2x = -4.83×10^{-5}*
E.	*less…*	*2.41×10^{-5} M*	*Eqm = $[Cl^-]_{eqm}$*

Precipitation leads to eqm being established:
$1.6\times10^{-5} = (2.41\times10^{-5})([Cl^-]_{eqm})^2$
$([Cl^-]_{eqm})^2 = 0.6639$
$[Cl^-]_{eqm} = 0.8148$ M

So: $[Cl^-]_{initial} = [Cl^-]_{eqm} + 4.83\times10^{-5}$ M
$= 0.8148 + 4.83\times10^{-5}$ M
≈ 0.8148 M

To treat 500 L wastewater:
n_{NaCl} = (500 L)(0.8148 M)
= 407 mol NaCl required
m_{NaCl} = 407 mol x 58.45 g/mol
= 23800 g
≈ 24 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:

a) 15 M $NH_3(aq)$
b) 12 M HCl(aq)
c) $NH_4Cl(s)$
d) Pure ("glacial") acetic acid, $HC_2H_3O_2$

SUBSTANCE	K_a
HCl	very large
$HC_2H_3O_2$	1.8×10^{-5}
NH_4^+	5.6×10^{-10}
H_2O	$K_w = 1\times10^{-14}$

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} $PbSO_4$ = 1.6×10^{-8}; K_{sp} $CaSO_4$ = 6.1×10^{-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.

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 $[HPO_4^{2-}] / [H_2PO_4^-]$ in this buffer?

a) **(6 marks)** To mimic blood, the buffer must exert an osmotic pressure of π = 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.