Lecture 17 CH131 Summer 1

Thursday, June 20, 2019

Chapter 16: Solubility equilibria …
- Solubility equilibria
- Practice with solubility equilibria

Course evaluation

Begin ch16: Electron transfer reactions and electrochemistry.
- Balancing redox equations, http://goo.gl/MMEUCs

Next lecture: Continue ch16

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Ch15: Solubility, precipitation, and complexation

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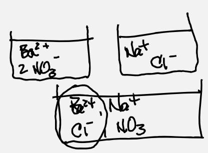
Solubility equilibria

$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2\,X^{-}(aq),\ K = K_{sp}$

Five kinds of problems
1. From solubility → get K_{sp}
2. From K_{sp} → get solubility
3. Solubility in presence of common ion
4. Will precipitation occur?
5. What remains after precipitation?



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1. From K_{sp} → get solubility

What is the molar solubility of CaF_2? $K_{sp} = 3.9 \times 10^{-11}$

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^{-}(aq)$

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1. From K_{sp} → get solubility

What is the molar solubility of CaF_2? $K_{sp} = 3.9 \times 10^{-11}$

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$

	MX_2	M^{2+}	X^-
Initial	excess	0	0
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$2x$

Q

$0 < K_{sp}$

$K_{sp} = (x)(2x)^2 = 4x^3 \quad x = \sqrt[3]{K_{sp}/4}$

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1. From K_{sp} → get solubility

What is the molar solubility of CaF_2? $K_{sp} = 3.9 \times 10^{-11}$

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$

	MX_2	M^{2+}	X^-
Initial	excess	0	0
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$2x$

$K_{sp} = (M^{2+})(X^-)^2 = (x)(2x)^2 = 4x^3$

Answer: 0.00021 mol/L

Check: $0.00021 \times (2 \times 0.00021)^2 = 3.9 \times 10^{-11} = K_{sp}$

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2. From solubility → get K_{sp}

The solubility of magnesium phosphate is 0.000259 g/100 g of water at 20 °C. Calculate its K_{sp} at this temperature.

$Mg_3(PO_4)_2\,(s) \rightleftharpoons 3\,Mg^{2+}(aq) + 2\,PO_4^{3-}(aq)$ ($-x$, $3x$, $2x$)

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$Mg_3(PO_4)_2\,(s) \rightleftharpoons 3\,Mg^{2+}(aq) + 2\,PO_4^{3-}(aq)$

	M_3X_2	M^{2+}	X^{3-}
Initial	excess	0	0
Change			
Equilibrium			

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$$Mg_3(PO_4)_2\,(s) \rightleftharpoons 3\,Mg^{2+}(aq) + 2\,PO_4^{3-}(aq)$$

	M_3X_2	M^{2+}	X^{3-}
Initial	excess	0	0
Change	$-x$	$+3x$	$+2x$
Equilibrium	excess	$3x$	$2x$

$$0.000259\ \text{g}/100\ \text{g} \rightarrow \text{mol/L} = x$$

$$K_{sp} = (M^{2+})^3(X^{3-})^2 = (3x)^3(2x)^2 = 108\,x^5$$

Answer: 1.00×10^{-23}

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3. Solubility in presence of common ion

25°C

The molar solubility of CaF_2, $K_{sp} = 3.9 \times 10^{-11}$, is 0.00021 mol/L. Calculate the molar solubility in a solution of 0.015 M NaF.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

0.015 M $F^-(aq)$

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3. Solubility in presence of common ion

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$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	MX_2	M^{2+}	X^-
Initial			
Change			
Equilibrium			

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3. Solubility in presence of common ion

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$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	MX_2	M^{2+}	X^-
Initial	excess	0	$c_{ion} = 0.015$
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$0.015 + 2x \approx 0.015$

$$K_{sp} = [Ca^{2+}][F^-]^2 = x\,(0.015)^2$$

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3. Solubility in presence of common ion

The molar solubility of CaF_2, $K_{sp} = 3.9 \times 10^{-11}$, is 0.00021 mol/L. Calculate the molar solubility in a solution of 0.015 M NaF.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	MX_2	M^{2+}	X^-
Initial	excess	0	c_{ion}
Change	$-x$	$+x$	$+2x$
Equilibrium	excess	x	$c_{ion} + 2x \approx c_{ion}$

$K_{sp} = (M^{2+})(X^-)^2 = (x)(c_{ion})^2$

Large c_{ion} makes x smaller

Answer: 1.7×10^{-7}, 0.08 % of the value in pure water!

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4. Will precipitation occur?

0.2 mmol of NaF and 10 mmol of $Ca(NO_3)_2$ are combined in a total volume of 1 L of water. Will a precipitate form? The K_{sp} of CaF_2 is 3.9×10^{-11}.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	MX_2	M^{2+}	X^-
Initial			

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4. Will precipitation occur?

0.2 mmol of NaF and 10 mmol of $Ca(NO_3)_2$ are combined in a total volume of 1 L of water. Will a precipitate form? The K_{sp} of CaF_2 is 3.9×10^{-11}.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	MX_2	M^{2+}	X^-
Initial	0	c_M	c_X

Is $(M^{2+})(X^-)^2 = (c_M)(c_X)^2 = Q_{sp} > K_{sp}$?

If no, then no precipitation.

If yes, then a precipitate will form.

Answer: $Q_{sp} = 4 \times 10^{-10} > K_{sp}$, so $CaF_2(s)$ will precipitate

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5. What remains after precipitation

When 0.2 mmol of NaF and 10 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution? K_{sp} of CaF_2 is 3.9×10^{-11}.

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5. What remains after precipitation

When 0.2 mmol of NaF and 10 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
The K_{sp} of CaF_2 is 3.9 x 10^{-11}.

	MX_2	M^{2+}	X^-
Initial mol			
Revised M			
Change			
Equilibrium			

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5. What remains after precipitation

When 0.2 mmol of NaF and 10.0 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
The K_{sp} of CaF_2 is 3.9 x 10^{-11}.

	MX_2	M^{2+}	X^-
Initial mol	0	0.0100 mol	0.0002 mol
Revised M			
Change			
Equilibrium			

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5. What remains after precipitation

When 0.2 mmol of NaF and 10.0 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
The K_{sp} of CaF_2 is 3.9 x 10^{-11}.

	MX_2	M^{2+}	X^-
Initial mol	0	0.0100 mol	0.0002 mol
Revised M	0.0001 mol	0.0099 mol/V	0
Change			
Equilibrium			

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5. What remains after precipitation

When 0.2 mmol of NaF and 10.0 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
The K_{sp} of CaF_2 is 3.9 x 10^{-11}.

	MX_2	M^{2+}	X^-
Initial	0	0.0100 mol	0.0002 mol
Revised	0.0001 mol	0.0099 mol/V	0/V
Change	$-y$	$+y$	$+2y$
Equilibrium			

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5. What remains after precipitation

When 0.2 mmol of NaF and 10.0 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
The K_{sp} of CaF_2 is 3.9 x 10^{-11}.

	MX_2	M^{2+}	X^-
Initial	0	0.0100 mol	0.0002 mol
Revised	0.0001 mol	0.0099 mol/V	0/V
Change	$-y$	$+y$	$+2y$
Equilibrium	≈ 0.0001 mol	≈ 0.0099 mol/V	$2y$

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5. What remains after precipitation

When 0.2 mmol of NaF and 10.0 mmol of $Ca(NO_3)_2$ are combined in 1 L of water, $CaF_2(s)$ precipitates. How much Ca^{2+} and F^- remain in solution?
The K_{sp} of CaF_2 is 3.9 x 10^{-11}.

	MX_2	M^{2+}	X^-
Initial	0	0.0100 mol	0.0002 mol
Revised	0.0001 mol	0.0099 mol/V	0/V
Change	$-y$	$+y$	$+2y$
Equilibrium	≈ 0.0001 mol	≈ 0.0099 mol/V	$2y$

$$K_{sp} = (M^{2+})(X^-)^2 \approx (0.0099)\,(2\,y)^2$$

Answer: $[Ca^{2+}] = 0.0099$ M, $[F^-] = 2\,y = 0.000063$ M

Check: $Q_{sp} = (0.0099)(0.000063)^2 = 3.9 \times 10^{-11} = K_{sp}$

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Practice with solubility equilibria

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Precipitation on mixing

$PbI_2(s)$ $K_{sp} = 9.8 \times 10^{-9}$ M^3

$Pb^{2+} = 0.120$ mol

$[Pb^{2+}]_0 = 2.00$ M

$I^- = 4.00 \times 10^{-5}$ mol

$[I^-]_0 = 6.70 \times 10^{-4}$ M

$Q_{sp} = 8.9 \times 10^{-7} M^3 > K_{sp}$, so precipitate will form

22-35. If we mix 40.0 mL of 3.00 M $Pb(NO_3)_2(aq)$ with 20.0 mL of 2.00 × 10^{-3} M NaI(*aq*), does $PbI_2(s)$ precipitate from the solution? If yes, then calculate how many moles of $PbI_2(s)$ precipitate and the values of $[Pb^{2+}]$, $[I^-]$, $[NO_3^-]$, and $[Na^+]$ at 25°C at equilibrium.

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

Be sure to use the net ionic equation only,

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$

Do not use

$Pb(NO_3)_2(aq) + 2\,NaI(aq) \rightleftharpoons PbI_2(s) + 2\,Na^+(aq) + 2\,NO_3^-(aq)$

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Precipitation on mixing

$Pb^{2+} = 0.120$ mol

$[Pb^{2+}]_0 = 2.00$ M

$I^- = 4.00 \times 10^{-5}$ mol

22-35. If we mix 40.0 mL of 3.00 M $Pb(NO_3)_2(aq)$ with 20.0 mL of 2.00×10^{-3} M $NaI(aq)$, does $PbI_2(s)$ precipitate from the solution? If yes, then calculate how many moles of $PbI_2(s)$ precipitate and the values of $[Pb^{2+}]$, $[I^-]$, $[NO_3^-]$, and $[Na^+]$ at 25°C at equilibrium.

	$[AX_2]$/M	$[A^{2+}]$/M	$[X^-]$/M
Initial mol	0	0.0120 mol	0.0000400 mol
Revised […]	0.0000200 mol	≈ 0.0120 mol/V = 2.00	0/V
Change	$-y$	$+y$	$+2y$
Equilibrium	≈ 0.0001 mol	≈ 2.00	$2y$

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Precipitation on mixing

$K_{sp} = (2.00M)(2y)^2$

$y = 3.5 \times 10^{-5}$ M

$PbI_2(s) = 0.0000200 - y \times 0.060$ L

$= 1.8 \times 10^{-5}$ mol

22-35. If we mix 40.0 mL of 3.00 M $Pb(NO_3)_2(aq)$ with 20.0 mL of 2.00×10^{-3} M $NaI(aq)$, does $PbI_2(s)$ precipitate from the solution? If yes, then calculate how many moles of $PbI_2(s)$ precipitate and the values of $[Pb^{2+}]$, $[I^-]$, $[NO_3^-]$, and $[Na^+]$ at 25°C at equilibrium.

	$[AX_2]$/M	$[A^{2+}]$/M	$[X^-]$/M
Initial mol	0	0.0120 mol	0.0000400 mol
Revised […]	0.0000200 mol	≈ 0.0120 mol/V = 2.00	0/V
Change	$-y$	$+y$	$+2y$
Equilibrium	1.8×10^{-5}mol	≈ 2.00	7.0×10^{-5}

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[TP] The expression for the equilibrium constant for the solubility equilibrium $M_2X(s) \rightleftharpoons 2\ M^+(aq) + X^{2-}(aq)$ is …

0% 1. $K_{sp} = (2\ M^+)\ (X^{2-})\ /\ (M_2X)$
0% 2. $K_{sp} = (2\ M^+)^2\ (X^{2-})\ /\ (M_2X)$
0% 3. $K_{sp} = (2\ M^+)^2\ (X^{2-})$
100% 4. $K_{sp} = (M^+)^2\ (X^{2-})$

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[TP] K_{sp} for $M_2X(s) \rightleftharpoons 2\ M^+(aq) + X^{2-}(aq)$ is 8×10^{-11}. Assume a maximum of y moles of $M_2X(s)$ can dissolve in one liter. What is true for y?

0% 1. $K_{sp} = (2\ y)\ (y)$
92% 2. $K_{sp} = (2\ y)^2\ (y)$
8% 3. $K_{sp} = (y)^2\ (y)$
0% 4. None of the above

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[Quiz] K_{sp} for $M_2X(s) \rightleftharpoons 2\,M^+(aq) + X^{2-}(aq)$ is 8×10^{-11}. Assume a maximum of y moles of $M_2X(s)$ can dissolve in one liter. What is true for y if $M^+(aq)$ is initially 0.1 M (that is, M^+ is a common ion)?

0%	1.	$K_{sp} \approx (2 \times 0.1)\,(y)$
8%	2.	$K_{sp} \approx (2 \times 0.1)^2\,(y)$
85%	3.	$K_{sp} \approx (0.1)^2\,(y)$
8%	4.	$K_{sp} \approx (0.1)\,(y)$
0%	5.	None of the above

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Online course evaluation

- bu.campuslabs.com/courseeval
- Use BU login and Kerberos password
- Anonymous and seen by instructors only after grades submitted
- Comments in text fields especially valued and encouraged.
- Please try to answer all questions
- When done, please close your browser

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A long time ago …

… my chemistry teacher (John Endicott) ended a lecture by asking us to balance a chemical equation like the following.

$$O_2(g) + NO(g) \rightarrow H_2O_2(aq) + NO_3^-(aq)$$

I tried by inspection, but could not do it.

half-reaction $\left\{ \begin{array}{l} NO \rightarrow NO_3^- \\ O_2 \rightarrow H_2O_2 \end{array} \right.$ oxidation, e^- released; reduction, e^- consumed

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Balancing half-reactions

For oxidation numbers and balancing redox equations, please work through http://goo.gl/MMEUCs

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Balancing oxidation reduction equations

For each oxidation reduction pair (half-reactions)

1. Balance elements other than O and H
2. Balance O with $H_2O(l)$
3. Balance H with $H^+(aq)$ (not H_3O^+)
4. Balance charge by adding e^- to the side that is most positive

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Balancing oxidation reduction equations

Balance $P_4(s) \rightarrow H_3PO_4(aq)$

Answer: $16\ H_2O(l) + P_4(s) \rightarrow 4\ H_3PO_4(aq) + 20\ H^+(aq) + 20\ e^-$

oxidation, e^- released

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Balancing oxidation reduction equations

Balance $S_2O_8^{2-}(aq) \rightarrow HSO_4^-(aq)$

Answer: $2\ e^- + 2\ H^+(aq) + S_2O_8^{2-}(aq) \rightarrow 2\ HSO_4^-(aq)$

reduction, e^- consumed

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Balancing oxidation reduction equations

Combine balanced half-reactions

1. Adjusts e^- to be the same
2. Combine
3. Cancel where possible

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Balancing oxidation reduction equations

Combine balanced half-reactions

$16\ H_2O(l) + P_4(s) \rightarrow 4\ H_3PO_4(aq) + 20\ H^+(aq) + 20\ e^-$

$2\ e^- + 2\ H^+(aq) + S_2O_8^{2-}(aq) \rightarrow 2\ HSO_4^-(aq)$

$16\ H_2O(l) + P_4(s) + 10\ S_2O_8^{2-}(aq) \rightarrow 4\ H_3PO_4(aq) + 20\ HSO_4^-(aq)$

$O_2 + NO \rightarrow H_2O_2 + NO_3^-$

$3\ (2e^- + 2H^+ + O_2 \rightarrow H_2O_2)$

$(2H_2O + NO \rightarrow NO_3^- + 4H^+ + 3e^-)\ 2$

$6H^+ + 3O_2 \rightarrow 3H_2O_2$

$4H_2O + 2NO \rightarrow 2NO_3^- + 8H^+$

$3O_2 + 4H_2O + 2NO \rightarrow 3H_2O_2 + 2NO_3^- + 2H^+$

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