

Lecture 21 CH102 A1 (MWF 9:05 am) Spring 2018 Copyright © 2018 Dan Dill dan@bu.edu

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

25% 1. $K_{sp} = (2 M^+) (X^{2-}) / (M_2X)$
 25% 2. $K_{sp} = (2 M^+)^2 (X^{2-}) / (M_2X)$
 25% 3. $K_{sp} = (2 M^+)^2 (X^{2-})$
 25% 4. $K_{sp} = (M^+)^2 (X^{2-})$

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Response Counter

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Friday, March 16, 2018

- Review: $[H_3O^+]$ when different amounts of “not enough” base added

Ch15: Solubility, precipitation, and complexation

- Five kinds of solubility equilibria problems

Next lecture: Complete ch15: Practice with solubility equilibria; Begin ch16: Electron transfer reactions and electrochemistry.

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Different amounts of “not enough” base

At 25 °C, the pH of a 1.0 L solution of $c_a = c_b = 1.00$ M, $K_a = 1 \times 10^{-5}$ is ...
pH = 5.00

Add 100. mL of 0.100 M NaOH ...

HA \rightarrow 1.00 mol - 0.010 mol = 0.99 mol
 A⁻ \rightarrow 1.00 mol + 0.010 mol = 1.01 mol
 \downarrow HA(aq) + OH⁻(aq) \rightarrow H₂O(l) + \uparrow A⁻(aq)

The pH of a 1.0 L solution of $c_a = 0.99$ mol/1.10 L, $c_b = 1.01$ mol/1.10 L is ...
 $c_a/c_b = 1.00 \rightarrow 0.99/1.01$, pH $\rightarrow 5.01$ (tiny change!)

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Different amounts of “not enough” base

At 25 °C, the pH of a 1.0 L solution pure water, $K_a = 1 \times 10^{-14}$ is ...
pH = 7.00

Add 100. mL of 0.100 M NaOH ...

$[OH^-] = 0.010$ mol/1.10 L = 0.0091
 pOH = 2.04, pH = 11.96 (huge change!)

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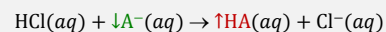
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Different amounts of “not enough” base

At 25 °C, the pH of a 1.0 L solution of $c_a = c_b = 1.00$ M, $K_a = 1 \times 10^{-5}$ is ...
pH = 5.00

Add 100. mL of 0.100 M HCl ...



The pH of a 1.0 L solution of $c_a = 1.01$ mol/1.10 L, $c_b = 0.99$ mol/1.10 L ...

$c_a/c_b = 1.00 \rightarrow 1.01/0.99$, pH $\rightarrow 4.99$ (tiny change!)



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Different amounts of “not enough” base

At 25 °C, the pH of a 1.0 L solution pure water, $K_a = 1 \times 10^{-14}$ is ...
pH = 7.00

Add 100. mL of 0.100 M HCl ...

$$[\text{H}_3\text{O}^+] = 0.010 \text{ mol}/1.10 \text{ L} = 0.0091$$

pH = 2.04 (huge change!)



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Buffers

Mixtures of a weak acid and its conjugate base (or weak base and its conjugate acid) exhibit the special property that they **resist changes to pH**.

For this reason such mixtures are known as **buffers**.

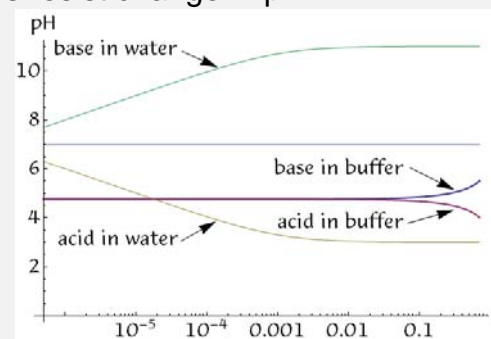


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Buffers resist change in pH



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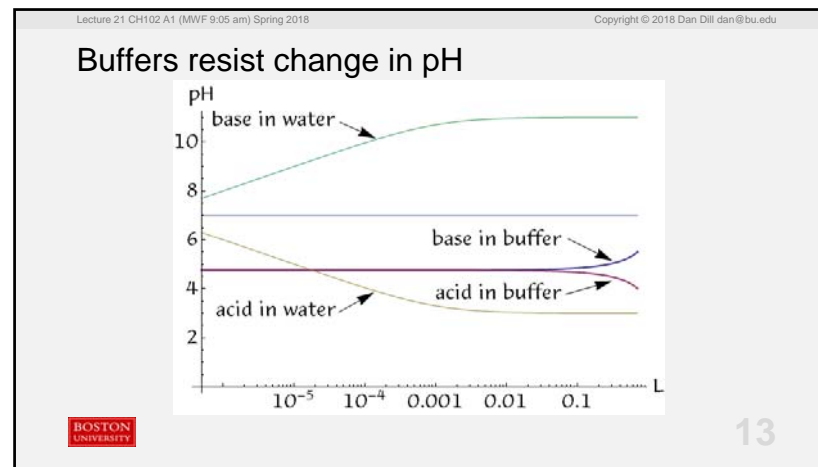
Buffers resist change in pH

Added strong base (say, OH^-) is gobbled up ...
 $\downarrow \text{HA}(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \uparrow \text{A}^-(aq)$
 c_a lowered, c_b raised, c_a/c_b lowered

Added strong acid (say, HCl) is gobbled up ...
 $\text{HCl}(aq) + \uparrow \text{A}^-(aq) \rightarrow \uparrow \text{HA}(aq) + \text{Cl}^-(aq)$
 c_b lowered, c_a raised, c_a/c_b raised

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Ch15: Solubility, precipitation, and complexation

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Solubility equilibria

$$\text{MX}_2(s) \rightleftharpoons \text{M}^{2+}(aq) + 2 \text{X}^-(aq), K = K_{sp}$$

Five kinds of problems

1. From solubility \rightarrow get K_{sp}
2. From $K_{sp} \rightarrow$ get solubility
3. Solubility in presence of common ion
4. Will precipitation occur?
5. What remains after precipitation?

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[TP] At 25 °C, K_{sp} of CaF_2 is 3.9×10^{-11} . What is the maximum number of moles of CaF_2 that can dissolve in water at 25 °C?

17% 1. 0.002
 17% 2. 0.01
 17% 3. 0.0002
 17% 4. 0.001
 17% 5. 0.00002
 17% 6. 0.0001

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1. From $K_{sp} \rightarrow$ get solubility

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

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

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1. From $K_{sp} \rightarrow$ get solubility

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

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

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

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1. From $K_{sp} \rightarrow$ get solubility

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

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^{-}(aq)$$

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

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

Answer: 0.00021 mol/L

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

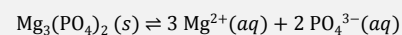
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2. From solubility → get K_{sp}

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



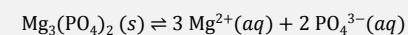
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2. From solubility → get K_{sp}

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Calculate its K_{sp} at this temperature.



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



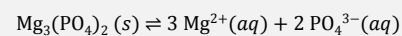
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The solubility of magnesium phosphate is 0.000259 g/100 g of water at 20 °C.
Calculate its K_{sp} at this temperature.



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

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

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

$$\text{Answer: } 1.00 \times 10^{-23}$$



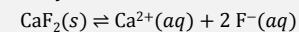
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3. Solubility in presence of common ion

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.



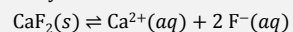
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	MX_2	M^{2+}	X^{-}
Initial			
Change			
Equilibrium			



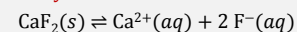
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	MX_2	M^{2+}	X^{-}
Initial	excess	0	c_{ion}
Change			
Equilibrium			



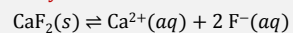
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Calculate the molar solubility in a solution of 0.015 M NaF.



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

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

Large c_{ion} makes x smaller

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



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