

Slides on solubility and precipitation, CH102 Spring 2016 Copyright © 2016 Dan Dill dan@bu.edu

Solubility equilibria

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

Five kinds of problems

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

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

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

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

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

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

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

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.

$$\text{Mg}_3(\text{PO}_4)_2 \rightleftharpoons 3 \text{Mg}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq})$$


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



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| | 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 g / 100 g → mol/L = x

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

Answer: 1.00×10^{-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.

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


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

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| | 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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4. Will precipitation occur?

0.2 mmol of NaF and 10 mmol of $\text{Ca}(\text{NO}_3)_2$ 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} .

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

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| | MX_2 | M^{2+} | X^- |
|---------|---------------|-----------------|--------------|
| Initial | | | |

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

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

If no, then no precipitation.
 If yes, then a precipitate will form.

Answer: $Q_{sp} = 4 \times 10^{-10} > K_{sp}$, so $\text{CaF}_2(s)$ will precipitate

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5. What remains after precipitation

When 0.2 mmol of NaF and 10 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1 L of water, $\text{CaF}_2(s)$ precipitates. **How much Ca^{2+} and F^- remain in solution?** The K_{sp} of CaF_2 is 3.9×10^{-11} .

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

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When 0.2 mmol of NaF and 10 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1 L of water, $\text{CaF}_2(\text{s})$ precipitates. **How much Ca^{2+} and F^- remain in solution?** The K_{sp} of CaF_2 is 3.9×10^{-11} .

| | MX_2 | M^{2+} | X^- |
|-------------|---------------|-----------------|---------------------------------|
| Initial | 0 | c_{M} | $c_{\text{X}} < 2 c_{\text{M}}$ |
| Revised | | | |
| Change | | | |
| Equilibrium | | | |



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| | MX_2 | M^{2+} | X^- |
|-------------|---------------|-----------------------------------|---------------------------------|
| Initial | 0 | c_{M} | $c_{\text{X}} < 2 c_{\text{M}}$ |
| Revised | excess | $c_{\text{M}} - 1/2 c_{\text{X}}$ | 0 |
| Change | | | |
| Equilibrium | | | |



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| | MX_2 | M^{2+} | X^- |
|-------------|---------------|-----------------------------------|---------------------------------|
| Initial | 0 | c_{M} | $c_{\text{X}} < 2 c_{\text{M}}$ |
| Revised | excess | $c_{\text{M}} - 1/2 c_{\text{X}}$ | 0 |
| Change | -y | +y | +2y |
| Equilibrium | | | |



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When 0.2 mmol of NaF and 10 mmol of $\text{Ca}(\text{NO}_3)_2$ are combined in 1 L of water, $\text{CaF}_2(\text{s})$ precipitates. **How much Ca^{2+} and F^- remain in solution?** The K_{sp} of CaF_2 is 3.9×10^{-11} .

| | MX_2 | M^{2+} | X^- |
|-------------|---------------|---|---------------------------------|
| Initial | 0 | c_{M} | $c_{\text{X}} < 2 c_{\text{M}}$ |
| Revised | excess | $c_{\text{M}} - 1/2 c_{\text{X}}$ | 0 |
| Change | -y | +y | +2y |
| Equilibrium | excess | $c_{\text{M}} - 1/2 c_{\text{X}} + y \approx c_{\text{M}} - 1/2 c_{\text{X}}$ | 2y |

$$K_{\text{sp}} = (\text{M}^{2+})(\text{X}^-)^2 \approx (c_{\text{M}} - 1/2 c_{\text{X}})(2y)^2$$

Answer: $[\text{Ca}^{2+}] = (c_{\text{M}} - 1/2 c_{\text{X}}) = 9.9 \text{ mmol}$, $[\text{F}^-] = 2y = 0.063 \text{ mmol}$

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



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