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Solubility equilibria

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

Five kinds of problems

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

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

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

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

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

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

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

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

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

Answer: 0.00021 mol/L

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

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

	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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The molar solubility of CaF_2 , $K_{\text{sp}} = 3.9 \times 10^{-11}$, is 0.00021 mol/L.
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$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^-(aq)$$

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

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

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

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

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

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

	MX_2	M^{2+}	X^{-}
Initial	0	c_{M}	c_{X}

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

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

Answer: $Q_{\text{sp}} = 4 \times 10^{-10} > K_{\text{sp}}$, so $\text{CaF}_2(\text{s})$ **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, $\text{CaF}_2(\text{s})$ 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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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, $\text{CaF}_2(\text{s})$ 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	$c_{\text{M}} - \frac{1}{2} c_{\text{X}}$	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	$c_{\text{M}} - \frac{1}{2} c_{\text{X}}$	0
Change	$-y$	$+y$	$+2y$
Equilibrium			

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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, $\text{CaF}_2(\text{s})$ 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	$c_{\text{M}} - \frac{1}{2} c_{\text{X}}$	0
Change	$-y$	$+y$	$+2y$
Equilibrium	excess	$c_{\text{M}} - \frac{1}{2} c_{\text{X}} + y \approx c_{\text{M}} - \frac{1}{2} c_{\text{X}}$	$2y$

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

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

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

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