Topic 7.11: Introduction to Solubility Equilibria

Worksheet · AP Chemistry

UNIT 7 · EQUILIBRIUM

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How to Use This Worksheet

Work in order. Section A checks the foundations: writing Ksp expressions, the bookkeeping that links molar solubility to each ion concentration, and the three Qsp cases. Section B practises the two calculation directions, Ksp from solubility and solubility from Ksp, a fair comparison between two salts, and a precipitation prediction. Section C is exam style: a solubility quoted in grams per litre, a mixing problem where the precipitate does not form, and the four-ion case of $Fe(OH)_3$.

Reference facts. Ksp is the equilibrium constant for a solid dissolving into its ions, with the solid itself omitted. Each ion concentration is raised to its coefficient in the dissolution equation. Molar solubility s is in mol/L; ion concentrations are s times the ion's coefficient. The patterns are

$Ksp = s^2$ for a 1:1 salt

$Ksp = 4s^3$ for a 1:2 or 2:1 salt

$Ksp = 27s^4$ for a 1:3 salt

Qsp less than Ksp is unsaturated, Qsp equal to Ksp is saturated, Qsp greater than Ksp precipitates until Qsp falls back to Ksp. Mixing dilutes: equal volumes halve each ion concentration before Qsp is computed. Ksp ranks solubility directly only between salts of the same stoichiometry; otherwise compare molar solubilities. Values at 25 °C: AgCl Ksp = 1.8×10^{-10}, s = 1.3×10^{-5} M; CaF_2 Ksp = 3.9×10^{-11}, s = 2.1×10^{-4} M; $BaSO_4$ Ksp = 1.1×10^{-10}, s = 1.0 ×

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10^{-5} M; $Mg(OH)_2$ Ksp = 5.6×10^{-12}, s = 1.1×10^{-4} M; PbI_2 Ksp = 9.8×10^{-9}, s = 1.3×10^{-3} M; $Fe(OH)_3$ Ksp = 2.8×10^{-39}, s = 1.0×10^{-10} M; $PbCl_2$ Ksp = 1.6×10^{-5}.

Three habits protect every answer. Write the ion concentrations in terms of s, multipliers included, before substituting numbers. Check the stoichiometry before you compare two salts, and never rank solubilities from Ksp across different stoichiometries. And use the concentrations in the mixture, after any dilution, when you compute Qsp.

Do not look at the answer key until you have attempted every question.

Section A: Recall and Concepts

A1. Write the Ksp expression for each dissolution, and in each case state why the solid does not appear. (a) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$. (b) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$. (c) $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$. (d) $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$.

A2. Judge each statement, giving the correction. (a) "Ksp for AgCl is $[Ag^+][Cl^-]$ divided by [AgCl], because the solid is a reactant." (b) "A salt with Ksp = 1.0×10^{-12} must be less soluble than a salt with Ksp = 1.0×10^{-10}." (c) "If twice as much solid is stirred into a saturated solution, the molar solubility doubles." (d) "Qsp = Ksp means the solution is supersaturated and a precipitate is about to form."

A3. (a) $Mg(OH)_2$ dissolves as $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$. If the molar solubility is s, state $[Mg^{2+}]$ and $[OH^-]$ in terms of s, and hence Ksp in terms of s. (b) Do the same for $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$. (c) Do the same for $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$.

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A4. A solution of a salt's ions is tested with Qsp. State what each comparison means and what happens next. (a) Qsp greater than Ksp. (b) Qsp equal to Ksp. (c) Qsp less than Ksp. (d) In the cases where solid forms or dissolves, state the value Qsp moves toward.

A5. Ksp for AgCl is 1.8×10^{-10} and for CaF_2 is 3.9×10^{-11}. Their molar solubilities are 1.3×10^{-5} M and 2.1×10^{-4} M. (a) Which salt has the larger Ksp? (b) Which salt is more soluble? (c) Explain why the two answers differ. (d) Ksp for $BaSO_4$ is 1.1×10^{-10}. State which of AgCl and $BaSO_4$ is more soluble, and explain why this comparison is safe.

Section B: Core Practice

B1. The molar solubility of AgCl in pure water is 1.3×10^{-5} M. (a) State $[Ag^+]$ and $[Cl^-]$ in the saturated solution. (b) Calculate Ksp for AgCl. (c) Calculate the solubility of AgCl in g/L, given its molar mass is 143.32 g/mol. (d) Calculate the mass of AgCl that dissolves in 500 mL of water at saturation.

B2. The solubility of CaF_2 is 1.64×10^{-2} g/L. The molar mass of CaF_2 is 78.08 g/mol. (a) Convert the solubility to mol/L. (b) State $[Ca^{2+}]$ and $[F^-]$ in the saturated solution. (c) Calculate Ksp for CaF_2. (d) Check your answer with the $4s^3$ pattern.

B3. Ksp for $Mg(OH)_2$ is 5.6×10^{-12}. (a) Write Ksp in terms of the molar solubility s. (b) Calculate s. (c) State $[Mg^{2+}]$ and $[OH^-]$ in a saturated solution. (d) Calculate the solubility in g/L, given the molar mass of $Mg(OH)_2$ is 58.33 g/mol.

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B4. Ksp for AgCl is 1.8×10^{-10} and for Ag_2CrO_4 is 1.1×10^{-12}. (a) Calculate the molar solubility of each salt. (b) State which salt is more soluble in pure water, and by about what factor. (c) Explain why the Ksp order alone gives the wrong answer here. (d) State $[Ag^+]$ in a saturated solution of Ag_2CrO_4.

B5. Equal volumes of 0.0010 M $CaCl_2$ and 0.0010 M NaF are mixed. Ksp for CaF_2 is 3.9×10^{-11}. (a) State $[Ca^{2+}]$ and $[F^-]$ immediately after mixing. (b) Calculate Qsp. (c) State whether a precipitate of CaF_2 forms, and why. (d) As precipitation proceeds, state what happens to $[Ca^{2+}]$, to $[F^-]$, and to Qsp, and the value Qsp reaches when the changes stop. (e) State which ion concentration falls faster as precipitation proceeds, and why.

B6. Ksp for PbI_2 is 9.8×10^{-9}. (a) Write Ksp in terms of s. (b) Calculate the molar solubility of PbI_2. (c) State $[Pb^{2+}]$ and $[I^-]$ in a saturated solution. (d) Calculate the solubility in g/L, given the molar mass of PbI_2 is 461.0 g/mol. (e) Calculate the mass of PbI_2 that dissolves in 250 mL of water at saturation.

Section C: Exam Style

C1. The solubility of $CaCO_3$ in water is 6.9×10^{-3} g/L. The molar mass of $CaCO_3$ is 100.09 g/mol. (a) Convert the solubility to a molar solubility. (b) State $[Ca^{2+}]$ and $[CO_3^{2-}]$ in the saturated solution. (c) Calculate Ksp for $CaCO_3$. (d) Tables quote Ksp = 4.7×10^{-9} for $CaCO_3$. State whether your answer agrees, and explain any difference. (e) More solid $CaCO_3$ is added to the saturated solution and the mixture is stirred. State what happens to $[Ca^{2+}]$, and why.

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C2. A 100 mL sample of 0.0020 M $Pb(NO_3)_2$ is mixed with 100 mL of 0.0040 M KI. Ksp for PbI_2 is 9.8×10^{-9}. (a) State $[Pb^{2+}]$ and $[I^-]$ in the mixture. (b) Calculate Qsp and state whether PbI_2 precipitates. (c) The iodide concentration in the mixture is raised tenfold, to 0.020 M, with $[Pb^{2+}]$ unchanged. Calculate the new Qsp and state whether PbI_2 precipitates now. (d) The original mixture from part (a) is diluted with water to twice its volume. Calculate the new Qsp and state whether the conclusion changes. (e) Solid PbI_2 is added to the original mixture from part (a). State what happens to it, and why.

C3. Ksp for $Fe(OH)_3$ is 2.8×10^{-39}. (a) Write the Ksp expression and then Ksp in terms of the molar solubility s. (b) Calculate s. (c) State $[Fe^{3+}]$ and $[OH^-]$ in a saturated solution. (d) Calculate the mass of $Fe(OH)_3$ that dissolves in 1.0 L of water at saturation, given its molar mass is 106.87 g/mol. (e) Calculate the mass that dissolves in 10 L of water at saturation.

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Answer Key

A1. (a) Ksp = $[Ba^{2+}][SO_4^{2-}]$. (b) Ksp = $[Pb^{2+}][Cl^-]^2$, with the chloride concentration squared for its coefficient of 2. (c) Ksp = $[Ag^+]^2[CrO_4^{2-}]$, with the silver concentration squared. (d) Ksp = $[Fe^{3+}][OH^-]^3$, with the hydroxide concentration cubed. In every case the solid is omitted because a pure solid's amount does not enter the equilibrium expression; only dissolved ions appear, each raised to its coefficient.

A2. (a) False. The solid never appears in a Ksp expression: Ksp for AgCl is simply $[Ag^+][Cl^-]$. (b) False as stated. Ksp orders solubility only between salts of the same stoichiometry. A 1:2 salt with Ksp = 1.0×10^{-12} has s = cube root of (Ksp ÷ 4) = 6.3×10^{-5} M, while a 1:1 salt with Ksp = 1.0×10^{-10} has s = √Ksp = 1.0×10^{-5} M, so the smaller Ksp belongs to the more soluble salt. (c) False. Molar solubility is fixed by Ksp at that temperature. Extra solid cannot dissolve into a solution that is already saturated, so s is unchanged. (d) False. Qsp = Ksp is the definition of a saturated solution in equilibrium with its solid: stable, with no net precipitation or dissolving. Supersaturated is Qsp greater than Ksp.

A3. (a) Each formula unit that dissolves gives one Mg^{2+} and two OH^-, so $[Mg^{2+}]$ = s and $[OH^-]$ = 2s. Ksp = $[Mg^{2+}][OH^-]^2 = (s)(2s)^2 = 4s^3$. (b) $[Fe^{3+}]$ = s and $[OH^-]$ = 3s. Ksp = $[Fe^{3+}][OH^-]^3 = (s)(3s)^3 = 27s^4$. (c) $[Ag^+]$ = 2s and $[CrO_4^{2-}]$ = s. Ksp = $[Ag^+]^2[CrO_4^{2-}] = (2s)^2(s) = 4s^3$. The multiplier belongs to the concentration first; the power from the expression is applied to the whole term, multiplier included.

A4. (a) Qsp greater than Ksp: the solution holds more ions than saturation allows (supersaturated), so solid precipitates until Qsp falls to Ksp; the dissolved ion concentrations fall as the amount of solid grows. (b) Qsp equal to Ksp: the solution is exactly saturated; no net change, and any added solid stays undissolved. (c) Qsp less than Ksp: the solution is unsaturated; no precipitate forms, and added solid dissolves, raising Qsp toward Ksp until either saturation is reached or the solid runs out. (d) In both moving cases the destination is the same: Qsp = Ksp, with solid present.

A5. (a) AgCl has the larger Ksp: 1.8×10^{-10} against 3.9×10^{-11}. (b) CaF_2 is more soluble: 2.1×10^{-4} M against 1.3×10^{-5} M, about sixteen times as much. (c) The stoichiometries differ. For AgCl, Ksp = s^2, so s is a square root of Ksp. For CaF_2, Ksp = $4s^3$, so s is a cube root of Ksp ÷ 4, and a cube root of a tiny number is far larger than its square root. Ksp values can only be compared directly when the salts share the same ion ratio. (d) AgCl is more soluble: 1.3×10^{-5} M against 1.0×10^{-5} M for $BaSO_4$. The comparison is safe because both salts are 1:1, so both give s = √Ksp and the larger Ksp means the larger solubility.

B1. (a) AgCl dissolves 1:1, so $[Ag^+] = [Cl^-] = s = 1.3 \times 10^{-5}$ M. (b) Ksp = $[Ag^+][Cl^-] = (1.3 \times 10^{-5})(1.3 \times 10^{-5}) = 1.7 \times 10^{-10}$. (c) Solubility = s × molar mass = $(1.3 \times 10^{-5})(143.32) = 1.9 \times 10^{-3}$ g/L. (d) Mass in 500 mL = $(1.9 \times 10^{-3}$ g/L$)(0.500$ L$) = 9.3 \times 10^{-4}$ g.

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B2. (a) s = $1.64 \times 10^{-2} \div 78.08 = 2.1 \times 10^{-4}$ M. Dividing by the molar mass converts grams of CaF_2 per litre into moles per litre; every later step needs moles. (b) $[Ca^{2+}] = s = 2.1 \times 10^{-4}$ M and $[F^-] = 2s = 4.2 \times 10^{-4}$ M, because each dissolving formula unit releases two fluoride ions. (c) $K_{sp} = [Ca^{2+}][F^-]^2 = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = (2.1 \times 10^{-4})(1.76 \times 10^{-7}) = 3.7 \times 10^{-11}$. (d) The pattern agrees: $4s^3 = 4(2.1 \times 10^{-4})^3 = 4(9.3 \times 10^{-12}) = 3.7 \times 10^{-11}$.

B3. (a) $K_{sp} = (s)(2s)^2 = 4s^3$. (b) s = cube root of ($K_{sp} \div 4$) = cube root of $(5.6 \times 10^{-12} \div 4)$ = cube root of $1.4 \times 10^{-12} = 1.1 \times 10^{-4}$ M. (c) $[Mg^{2+}] = s = 1.1 \times 10^{-4}$ M and $[OH^-] = 2s = 2.2 \times 10^{-4}$ M. (d) Solubility = s × molar mass = $(1.1 \times 10^{-4})(58.33) = 6.4 \times 10^{-3}$ g/L.

B4. (a) AgCl: $s = \sqrt{K_{sp}} = \sqrt{(1.8 \times 10^{-10})} = 1.3 \times 10^{-5}$ M. Ag_2CrO_4: $K_{sp} = 4s^3$, so s = cube root of $(1.1 \times 10^{-12} \div 4)$ = cube root of $2.75 \times 10^{-13} = 6.5 \times 10^{-5}$ M. (b) Ag_2CrO_4 is more soluble, by a factor of $6.5 \times 10^{-5} \div 1.3 \times 10^{-5} = 5.0$. (c) The salts have different stoichiometries, so their Ksp values are built from different powers of s: a square for AgCl and a cube (times 4) for Ag_2CrO_4. A cube root of a very small number exceeds a square root of a somewhat larger one, so the Ksp ranking reverses when both are converted to molar solubility, the quantity that actually measures dissolving. (d) $[Ag^+] = 2s = 2 \times 6.5 \times 10^{-5} = 1.3 \times 10^{-4}$ M.

B5. (a) Mixing equal volumes halves each concentration: $[Ca^{2+}] = 0.00050$ M and $[F^-] = 0.00050$ M. (b) $Q_{sp} = [Ca^{2+}][F^-]^2 = (5.0 \times 10^{-4})(5.0 \times 10^{-4})^2 = (5.0 \times 10^{-4})(2.5 \times 10^{-7}) = 1.3 \times 10^{-10}$. (c) $Q_{sp} = 1.3 \times 10^{-10}$ exceeds $K_{sp} = 3.9 \times 10^{-11}$, so the mixture is supersaturated and CaF_2 precipitates until Qsp falls to Ksp. (d) Removing $CaF_2(s)$ takes one Ca^{2+} and two F^- out of solution per formula unit, so both concentrations fall, Qsp falls with them, and precipitation stops when Qsp reaches exactly $K_{sp} = 3.9 \times 10^{-11}$, with solid CaF_2 present: the saturated equilibrium. (e) $[F^-]$ falls twice as fast as $[Ca^{2+}]$, because each formula unit that precipitates removes two fluoride ions for every one calcium ion.

B6. (a) Dissolving s gives $[Pb^{2+}] = s$ and $[I^-] = 2s$, so $K_{sp} = (s)(2s)^2 = 4s^3$. (b) s = cube root of $(9.8 \times 10^{-9} \div 4)$ = cube root of $2.45 \times 10^{-9} = 1.3 \times 10^{-3}$ M. Check: $4(1.35 \times 10^{-3})^3 = 9.8 \times 10^{-9}$. (c) $[Pb^{2+}] = 1.3 \times 10^{-3}$ M and $[I^-] = 2s = 2.7 \times 10^{-3}$ M. (d) Solubility = $(1.35 \times 10^{-3})(461.0) = 0.62$ g/L, using the unrounded value of s from part (b). (e) Mass in 250 mL = (0.62 g/L)(0.250 L) = 0.16 g.

C1. (a) $s = 6.9 \times 10^{-3} \div 100.09 = 6.9 \times 10^{-5}$ M. (b) $CaCO_3$ dissolves 1:1, so $[Ca^{2+}] = [CO_3^{2-}] = 6.9 \times 10^{-5}$ M. (c) $K_{sp} = [Ca^{2+}][CO_3^{2-}] = (6.9 \times 10^{-5})^2 = 4.8 \times 10^{-9}$. (d) Yes, it agrees: the tabulated 4.7×10^{-9} differs only in the last digit, because the quoted solubility is given to two significant figures. Working backwards, $\sqrt{(4.7 \times 10^{-9})} = 6.9 \times 10^{-5}$ M, the value the question started from. (e) Nothing happens to $[Ca^{2+}]$. The solution is already saturated, so Qsp already equals Ksp and the added solid cannot dissolve; $[Ca^{2+}]$ stays at 6.9×10^{-5} M and the extra solid simply rests at the bottom.

C2. (a) Mixing equal volumes halves each concentration: $[Pb^{2+}] = 0.0010$ M and $[I^-] = 0.0020$ M. (b) $Q_{sp} = [Pb^{2+}][I^-]^2 = (0.0010)(0.0020)^2 = (0.0010)(4.0 \times 10^{-6}) = 4.0 \times 10^{-9}$. This is below $K_{sp} = 9.8 \times 10^{-9}$, so the mixture is unsaturated and no PbI_2 precipitates. (c) $Q_{sp} = (0.0010)(0.020)^2 = (0.0010)(4.0 \times 10^{-4}) = 4.0 \times 10^{-7}$, above $K_{sp} = 9.8 \times 10^{-9}$, so yellow PbI_2 precipitates. (d) Diluting twofold halves both concentrations again: $[Pb^{2+}] = 5.0 \times 10^{-4}$ M and $[I^-] = 0.0010$ M, so $Q_{sp} = (5.0 \times 10^{-4})(0.0010)^2 = 5.0 \times$

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10^{-10}, smaller still. The conclusion is unchanged: no precipitate. (e) The solid dissolves. Because Qsp is less than Ksp the solution is unsaturated, so PbI_2 dissolves, raising both ion concentrations, until Qsp reaches Ksp (the solution saturates) or the added solid has all dissolved.

C3. (a) Ksp = $[Fe^{3+}][OH^-]^3$. With $[Fe^{3+}]$ = s and $[OH^-]$ = 3s, Ksp = $(s)(3s)^3 = 27s^4$. (b) s = fourth root of (Ksp ÷ 27) = fourth root of $(2.8 \times 10^{-39} \div 27)$ = fourth root of $1.04 \times 10^{-40} = 1.0 \times 10^{-10}$ M. A fourth root can be taken as two square roots: $\sqrt{(1.04 \times 10^{-40})} = 1.02 \times 10^{-20}$, and $\sqrt{(1.02 \times 10^{-20})} = 1.0 \times 10^{-10}$. (c) $[Fe^{3+}] = s = 1.0 \times 10^{-10}$ M and $[OH^-] = 3s = 3.0 \times 10^{-10}$ M. (d) Mass dissolved per litre = s × molar mass $= (1.0 \times 10^{-10})(106.87) = 1.1 \times 10^{-8}$ g. (e) Mass in 10 L = $(1.1 \times 10^{-8}$ g/L)(10 L) $= 1.1 \times 10^{-7}$ g.

Continue Revising

Topic 7.11 Revision Notes

Topic 7.11 Quiz: Introduction to Solubility Equilibria

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Next Worksheet: Topic 7.12 Common-Ion Effect

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