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Topic 7.12: Common-Ion Effect

Worksheet · AP Chemistry

UNIT 7 · EQUILIBRIUM

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How to Use This Worksheet

Work in order. Section A checks the ideas: spotting a common ion, what adding one does to Qsp and Ksp, and how the ICE table is built when one ion starts with a head start. Section B practises the standard calculation in six versions: a 1:1 salt, a squared common ion, an exact quadratic solve, a hydroxide, a common cation in a different place, and a case where the approximation fails. Section C is exam style: a mixing problem, an approximation error judged honestly, and a comparison of how strongly two salts are suppressed.

Reference facts. A common ion is an ion shared between the sparingly soluble salt and another solute. Solubility with a common ion present is always lower than in pure water, and falls further as the common-ion concentration rises. Adding a common ion does not change Ksp. With the common ion at concentration C, solve $K_{sp} = s \times C^n$, where n is the exponent on the common ion. The common ion's equilibrium concentration is C plus its multiple of s. For a 1:1 salt, doubling C halves s; where the common ion is squared, doubling C cuts s by a factor of four. Ksp and pure-water s at 25 °C: AgCl 1.8×10^{-10} and 1.3×10^{-5} M; CaF_2 4.0×10^{-11} and 2.2×10^{-4} M; Ag_2CrO_4 1.1×10^{-12} and 6.5×10^{-5} M; $Ca(OH)_2$ 5.5×10^{-6} and 1.1×10^{-2} M; PbI_2 9.8×10^{-9} and 1.3×10^{-3} M; $BaSO_4$ 1.1×10^{-10} and 1.0×10^{-5} M; $Mg(OH)_2$ 5.6×10^{-12} and 1.1×10^{-4} M.

Three habits protect every answer. Write both ion concentrations in terms of s, the head start included, before substituting numbers. Run the 5 percent check on any approximation. Pause on every added species, name its ions, and check each against the dissolution equation before doing any arithmetic.

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

Section A: Recall and Concepts

A1. For each addition to a saturated solution, state the common ion, or state that there is none. (a) NaCl(aq) added to saturated AgBr(aq). (b) Na_2SO_4(aq) added to saturated $BaSO_4$(aq). (c) KNO_3(aq) added to saturated PbI_2(aq). (d) $AgNO_3$(aq) added to saturated Ag_2CrO_4(aq). (e) NaOH(aq) added to saturated $Mg(OH)_2$(aq).

A2. Judge each statement, giving the correction. (a) "Adding NaCl(aq) to a saturated AgCl solution lowers the Ksp of AgCl." (b) "Once the salt starts dissolving, the common ion's concentration stays exactly at its starting value C." (c) "A common ion at 0.10 M always cuts a salt's solubility by the same factor." (d) "Adding more solid to a common-ion solution raises the solubility back toward the pure-water value."

A3. PbI_2 is placed in KI(aq) in which $[I^-]$ starts at C. If the molar solubility of PbI_2 in this solution is s, state (a) $[Pb^{2+}]$ at equilibrium, (b) $[I^-]$ at equilibrium, (c) Ksp written in terms of s and C. (d) The same salt is placed instead in $Pb(NO_3)_2$(aq) in which $[Pb^{2+}]$ starts at C. State $[Pb^{2+}]$ and $[I^-]$ at equilibrium, and Ksp in terms of s and C.

A4. Solid NaCl is stirred into a saturated AgCl solution that already has solid AgCl present. (a) State what happens to Qsp at the moment of addition, and why. (b) State what the system then does. (c) State what happens to $[Ag^+]$, and what $[Cl^-]$ ends at compared with its value before the addition. (d) State the value Qsp has when the changes stop.

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A5. The molar solubility of AgCl is 1.3×10^{-5} M in pure water, 1.8×10^{-8} M in 0.010 M NaCl, and 1.8×10^{-9} M in 0.10 M NaCl. (a) Rank the three solutions by solubility. (b) For this 1:1 salt, state the factor by which s falls when $[Cl^-]$ rises by a factor of ten, and connect it to the form of the approximate equation $s \approx Ksp \div C$. (c) Predict the molar solubility of AgCl in 0.20 M NaCl. (d) State what happens to the solubility of AgCl in 0.10 M NaCl if the solution is diluted with an equal volume of pure water.

Section B: Core Practice

B1. Ksp for AgCl is 1.8×10^{-10}. (a) Write $[Ag^+]$ and $[Cl^-]$ in terms of s for AgCl dissolving in 0.050 M NaCl, and hence Ksp in terms of s. (b) Calculate s using the small-s approximation. (c) Run the check on the approximation. (d) By what factor is the solubility below its pure-water value of 1.3×10^{-5} M? (e) State $[Cl^-]$ at equilibrium.

B2. Ksp for PbI_2 is 9.8×10^{-9}. (a) Write Ksp in terms of s for PbI_2 dissolving in 0.050 M KI. (b) Calculate s using the small-s approximation. (c) Run the check on the approximation. (d) State $[Pb^{2+}]$ and $[I^-]$ at equilibrium. (e) State the factor by which the solubility falls short of the pure-water value of 1.3×10^{-3} M.

B3. Ksp for $BaSO_4$ is 1.1×10^{-10}. Calculate the molar solubility of $BaSO_4$ in 1.0×10^{-3} M Na_2SO_4 (a) by the small-s approximation, (b) exactly, by solving the quadratic, and (c) state the factor by which it falls short of the pure-water value of 1.0×10^{-5} M. (d) Run the check on the approximation. (e) State $[SO_4^{2-}]$ at equilibrium.

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B4. Ksp for $Mg(OH)_2$ is 5.6×10^{-12}. (a) Write Ksp in terms of s for $Mg(OH)_2$ dissolving in 0.10 M NaOH. (b) Calculate s using the small-s approximation. (c) Run the check on the approximation. (d) State the factor by which the solubility falls short of the pure-water value of 1.1×10^{-4} M. (e) State $[OH^-]$ at equilibrium.

B5. Ksp for Ag_2CrO_4 is 1.1×10^{-12}. Ag_2CrO_4 is dissolved in 0.010 M K_2CrO_4, so this time the common ion is CrO_4^{2-}. (a) Write $[Ag^+]$ and $[CrO_4^{2-}]$ in terms of s, and hence Ksp in terms of s. (b) Calculate s using the small-s approximation. (c) Run the check on the approximation. (d) State the factor by which the solubility falls short of the pure-water value of 6.5×10^{-5} M. (e) For comparison, Ag_2CrO_4 in 0.010 M $AgNO_3$ has s = 1.1×10^{-8} M. State which common ion suppresses the solubility more strongly at the same concentration, and explain the difference using the powers in the two Ksp expressions.

B6. Ksp for $PbCl_2$ is 1.6×10^{-5}, and its molar solubility in pure water is 1.6×10^{-2} M. $PbCl_2$ is placed in 0.010 M NaCl. (a) Write Ksp in terms of s and calculate the value the small-s approximation returns. (b) Show two separate reasons why that value cannot be trusted. (c) The exact root is s = 1.27×10^{-2} M. Verify it by back-substitution. (d) State the factor by which the common ion suppresses the solubility. (e) Explain why the suppression is so weak here.

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Section C: Exam Style

C1. A saturated AgCl solution, with $[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}$ M and solid present, is mixed with an equal volume of 0.20 M NaCl. Ksp for AgCl is 1.8×10^{-10}. (a) State $[Ag^+]$ and $[Cl^-]$ immediately after mixing, before any shift. (b) Calculate Qsp at that moment and state what happens next. (c) State $[Ag^+]$ and $[Cl^-]$ once equilibrium is reestablished. (d) Calculate how many moles of AgCl precipitate per litre of the mixture. (e) Calculate the mass of AgCl that precipitates per litre of the mixture, given its molar mass is 143.32 g/mol.

C2. Ksp for $Ca(OH)_2$ is 5.5×10^{-6}. $Ca(OH)_2$ is placed in 0.10 M NaOH. (a) Write Ksp in terms of s and calculate s using the small-s approximation. (b) Run the 5 percent check. (c) The exact root is $s = 5.4 \times 10^{-4}$ M. State the percentage error of the approximation and whether its direction matches the known bias of the method. (d) The solubility of $Ca(OH)_2$ in pure water is 1.1×10^{-2} M. State the suppression factor. (e) State $[OH^-]$ at equilibrium, using the exact root.

C3. AgCl in 0.10 M NaCl falls from 1.3×10^{-5} M to 1.8×10^{-9} M, a factor of about 7,000; CaF_2 in 0.010 M NaF falls from 2.2×10^{-4} M to 4.0×10^{-7} M, a factor of about 550. In pure saturated AgCl, $[Cl^-] = 1.3 \times 10^{-5}$ M; in pure saturated CaF_2, $[F^-] = 4.4 \times 10^{-4}$ M. (a) Confirm both factors from the solubilities given. (b) Show that each factor is close to (C divided by the common ion's concentration in the pure saturated solution) raised to the power of that ion in the Ksp expression. (c) Explain why AgCl is suppressed more strongly in the comparison that matters, even though its C is larger in absolute terms. (d) Predict the molar solubility of CaF_2 in 0.10 M NaF, and the suppression factor against pure water. (e) State which salt's suppression grows faster as C rises, and why.

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Answer Key

A1. (a) None: NaCl supplies Na^+ and Cl^-, while the AgBr equilibrium involves Ag^+ and Br^-. (b) SO_4^{2-}, present in both the added Na_2SO_4 and the $BaSO_4$ dissolution. (c) None: K^+ and NO_3^- appear nowhere in the PbI_2 equilibrium. (d) Ag^+, supplied by $AgNO_3$ and released by Ag_2CrO_4. (e) OH^-, supplied by NaOH and released by $Mg(OH)_2$.

A2. (a) False. Ksp is a constant at a fixed temperature and does not respond to added solute. The addition raises Qsp above Ksp; the solubility falls because the concentrations change. (b) False. The common ion's equilibrium concentration is C plus whatever the dissolving salt adds: C + s for Cl^- from AgCl, C + 2s for I^- from PbI_2. (c) False. The factor depends on C relative to the ion levels the salt produces alone, and on the power of the common ion: 0.10 M of Cl^- cuts AgCl's solubility about 7,000-fold, while 0.010 M of F^- cuts CaF_2's only about 550-fold. (d) False. A saturated solution cannot dissolve more solid at the same temperature; s is fixed by Ksp and C.

A3. (a) $[Pb^{2+}] = s$: lead ion comes only from the dissolving salt, one per formula unit. (b) $[I^-] = C + 2s$: the solution starts with C, and each formula unit adds two more. (c) $K_{sp} = [Pb^{2+}][I^-]^2 = s(C + 2s)^2$. The multiplier of 2 belongs to s before the square is applied. (d) $[Pb^{2+}] = C + s$ and $[I^-] = 2s$, so $K_{sp} = (C + s)(2s)^2 = 4s^2(C + s)$. The common ion sits in a different place, so the math changes with it.

A4. (a) Qsp jumps above Ksp: the added NaCl raises $[Cl^-]$ sharply while $[Ag^+]$ is momentarily unchanged, so $[Ag^+][Cl^-]$ exceeds 1.8×10^{-10}. (b) The system precipitates AgCl: Ag^+ and Cl^- leave the solution together as solid, in a 1:1 ratio. (c) $[Ag^+]$ falls steeply, by orders of magnitude. $[Cl^-]$ falls slightly but ends far above its value before the addition. (d) Precipitation stops when Qsp has fallen back to exactly Ksp, with solid AgCl present, but at a much lower $[Ag^+]$.

A5. (a) Pure water (1.3×10^{-5} M), then 0.010 M NaCl (1.8×10^{-8} M), then 0.10 M NaCl (1.8×10^{-9} M). (b) Each tenfold rise in $[Cl^-]$ cuts s tenfold: with $s \approx K_{sp} \div C$, multiplying C by 10 divides s by 10. That clean inverse pattern is special to the 1:1 case; where the common ion is squared, as for F^- in CaF_2, s falls with $1 \div C^2$ instead. (c) $s = K_{sp} \div C = (1.8 \times 10^{-10}) \div 0.20 = 9.0 \times 10^{-10}$ M. (d) Dilution halves $[Cl^-]$ to 0.050 M, so s rises to $(1.8 \times 10^{-10}) \div 0.050 = 3.6 \times 10^{-9}$ M: more solid dissolves.

B1. (a) $[Ag^+] = s$ and $[Cl^-] = 0.050 + s$, so $K_{sp} = s(0.050 + s)$. (b) Neglecting s beside 0.050: $s \approx (1.8 \times 10^{-10}) \div 0.050 = 3.6 \times 10^{-9}$ M. (c) The neglected term is s itself, 3.6×10^{-9} against C = 0.050: far under 5 percent. (d) Factor: $(1.3 \times 10^{-5}) \div (3.6 \times 10^{-9}) = 3{,}600$. (e) $[Cl^-] = 0.050 + s \approx 0.050$ M.

B2. (a) $[Pb^{2+}] = s$ and $[I^-] = 0.050 + 2s$, so $K_{sp} = s(0.050 + 2s)^2$. (b) Neglecting 2s beside 0.050: $s \approx (9.8 \times 10^{-9}) \div (0.050)^2 = (9.8 \times 10^{-9}) \div (2.5 \times 10^{-3}) = 3.9 \times 10^{-6}$ M. (c) $2s = 7.8 \times 10^{-6}$, 0.016 percent of 0.050: the check passes. (d) $[Pb^{2+}] = 3.9 \times 10^{-6}$ M and $[I^-] = 0.050 + 2s \approx 0.050$ M. (e) Factor: $(1.3 \times 10^{-3}) \div (3.9 \times 10^{-6}) = 330$.

B3. (a) Approximately: $K_{sp} = s(1.0 \times 10^{-3} + s)$; neglecting s gives $s \approx (1.1 \times 10^{-10}) \div (1.0 \times 10^{-3}) = 1.1 \times 10^{-7}$ M. (b) Exactly: $s^2 + (1.0 \times 10^{-3})s - 1.1 \times 10^{-10} = 0$, whose positive root is $s = 1.1 \times 10^{-7}$ M. (c)

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Factor: $(1.0 \times 10^{-5}) \div (1.1 \times 10^{-7}) = 91$. (d) The neglected term $s = 1.1 \times 10^{-7}$ M is 0.011 percent of C, far under the 5 percent limit. (e) $[SO_4^{2-}]$ at equilibrium is $1.0 \times 10^{-3} + s \approx 1.0 \times 10^{-3}$ M.

B4. (a) $[Mg^{2+}] = s$ and $[OH^-] = 0.10 + 2s$, so $K_{sp} = s(0.10 + 2s)^2$. (b) Neglecting 2s beside 0.10: $s \approx (5.6 \times 10^{-12}) \div (0.10)^2 = (5.6 \times 10^{-12}) \div 0.010 = 5.6 \times 10^{-10}$ M. (c) $2s = 1.1 \times 10^{-9}$, negligible beside 0.10. (d) Factor: $(1.1 \times 10^{-4}) \div (5.6 \times 10^{-10}) = 2.0 \times 10^5$. The tiny K_{sp} is the cause: in pure water $Mg(OH)_2$ produces only about 10^{-4} M of ions. (e) $[OH^-] = 0.10 + 2s \approx 0.10$ M.

B5. (a) The chromate starts with the head start: $[Ag^+] = 2s$ and $[CrO_4^{2-}] = 0.010 + s$, so $K_{sp} = (2s)^2(0.010 + s) = 4s^2(0.010 + s)$. (b) Neglecting s beside 0.010: $4s^2(0.010) = 1.1 \times 10^{-12}$, so $s^2 = (1.1 \times 10^{-12}) \div 0.040 = 2.75 \times 10^{-11}$ and $s = 5.2 \times 10^{-6}$ M. (c) The neglected term is $s = 5.2 \times 10^{-6}$ against C = 0.010, which is 0.052 percent: the check passes. (d) Factor: $(6.5 \times 10^{-5}) \div (5.2 \times 10^{-6}) = 13$. (e) The Ag^+ common ion suppresses far more strongly: $s = 1.1 \times 10^{-8}$ M against 5.2×10^{-6} M here. With Ag^+, $K_{sp} \approx C^2 s$ and s shrinks with $1 \div C^2$. With CrO_4^{2-}, $K_{sp} \approx 4s^2C$ and s shrinks with $1 \div \sqrt{C}$.

B6. (a) $[Pb^{2+}] = s$ and $[Cl^-] = 0.010 + 2s$, so $K_{sp} = s(0.010 + 2s)^2$. The approximation replaces $(0.010 + 2s)$ by 0.010: $s \approx (1.6 \times 10^{-5}) \div (0.010)^2 = (1.6 \times 10^{-5}) \div (1.0 \times 10^{-4}) = 0.16$ M. (b) First, 2s would be 0.32 M, thirty-two times the C it was supposed to be negligible beside. Second, 0.16 M exceeds $PbCl_2$'s solubility in pure water, 1.6×10^{-2} M. (c) With $s = 1.27 \times 10^{-2}$: $[Cl^-] = 0.010 + 2(1.27 \times 10^{-2}) = 0.0354$ M, and $K_{sp} = (1.27 \times 10^{-2})(0.0354)^2 = 1.6 \times 10^{-5}$. Confirmed. (d) Factor: $(1.6 \times 10^{-2}) \div (1.27 \times 10^{-2}) = 1.3$. (e) The suppression is feeble because $PbCl_2$'s own dissolving supplies 0.025 M of Cl^-, two and a half times the added head start.

C1. (a) Mixing equal volumes halves each concentration: $[Ag^+] = 6.5 \times 10^{-6}$ M and $[Cl^-] = 0.10$ M. (b) $Q_{sp} = (6.5 \times 10^{-6})(0.10) = 6.5 \times 10^{-7}$, far above $K_{sp} = 1.8 \times 10^{-10}$, so AgCl precipitates. (c) Precipitation removes Ag^+ and Cl^- in equal amounts; $[Cl^-]$ barely moves, so $[Ag^+]$ settles at $(1.8 \times 10^{-10}) \div 0.10 = 1.8 \times 10^{-9}$ M, with $[Cl^-] \approx 0.10$ M. (d) Silver precipitated per litre = $6.5 \times 10^{-6} - 1.8 \times 10^{-9} \approx 6.5 \times 10^{-6}$ mol. (e) Mass per litre = $(6.5 \times 10^{-6}$ mol$)(143.32$ g/mol$) = 9.3 \times 10^{-4}$ g.

C2. (a) $[Ca^{2+}] = s$ and $[OH^-] = 0.10 + 2s$, so $K_{sp} = s(0.10 + 2s)^2$. Neglecting 2s: $s \approx (5.5 \times 10^{-6}) \div (0.10)^2 = (5.5 \times 10^{-6}) \div 0.010 = 5.5 \times 10^{-4}$ M. (b) $2s = 1.1 \times 10^{-3}$, 1.1 percent of 0.10: inside the 5 percent limit. (c) Error: $(5.5 \times 10^{-4} - 5.4 \times 10^{-4}) \div (5.4 \times 10^{-4}) = 1.9$ percent, about 2 percent, and the approximation is the larger value, exactly the known bias. (d) Factor: $(1.1 \times 10^{-2}) \div (5.4 \times 10^{-4}) = 20$. (e) $[OH^-] = 0.10 + 2(5.4 \times 10^{-4}) = 0.10 + 1.1 \times 10^{-3} = 0.101$ M.

C3. (a) AgCl: $(1.3 \times 10^{-5}) \div (1.8 \times 10^{-9}) = 7{,}200$. CaF_2: $(2.2 \times 10^{-4}) \div (4.0 \times 10^{-7}) = 550$. (b) For AgCl: $C \div [Cl^-]$ in pure solution $= 0.10 \div (1.3 \times 10^{-5}) = 7{,}700$, to the power 1, giving about 7,700, close to 7,200. For CaF_2: $C \div [F^-]$ in pure solution $= 0.010 \div (4.4 \times 10^{-4}) = 23$, squared, giving about 520, close to 550. (c) What matters is not C itself but C measured against the ion level the salt reaches on its own, raised to the ion's power. AgCl's head start is thousands of times the level AgCl produces alone; CaF_2's smaller head start is only about twenty-three times its own fluoride level, and even squared it suppresses less. (d) In 0.10 M NaF, $s = K_{sp} \div C^2 = (4.0 \times 10^{-11}) \div (0.10)^2 = (4.0 \times 10^{-11}) \div 0.010 = 4.0 \times 10^{-9}$ M. The suppression factor is $(2.2 \times 10^{-4}) \div (4.0 \times 10^{-9}) = 55{,}000$. (e) CaF_2's suppression grows

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faster as C rises, because its common ion is squared: s falls with $1 \div C^2$, while AgCl's s falls only with $1 \div C$.

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