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Topic 7.13: pH and Solubility

Worksheet · AP Chemistry

UNIT 7 · EQUILIBRIUM

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How to Use This Worksheet

Work in order. Section A checks the definitions and the rules that decide whether a salt responds to pH at all. Section B practises the skills: converting pH to $[OH^-]$, finding the solubility of a hydroxide at a fixed pH, finding the pH at which a hydroxide first precipitates, and using Qsp to predict precipitation. Section C is exam style: judging claims and two full scenarios.

Reference facts. At 25 °C, pH + pOH = 14 and $[OH^-] = 10^{(-pOH)}$. For a hydroxide salt, $s = K_{sp}/[OH^-]^n$, where n is the number of hydroxide ions in the formula. Useful values: $Mg(OH)_2$, $K_{sp} = 5.6 \times 10^{-12}$, pure-water solubility $s = 1.1 \times 10^{-4}$ M and saturated-solution pH = 10.35; $Fe(OH)_3$, $K_{sp} = 2.8 \times 10^{-39}$; $Ca(OH)_2$, $K_{sp} = 5.5 \times 10^{-6}$. Precipitation begins when Qsp reaches Ksp. Ksp is fixed at a given temperature; only the solubility changes with pH. Salts of strong acids and strong bases (AgCl, $BaSO_4$, PbI_2) ignore pH entirely.

Three habits protect every answer. Convert pH to $[OH^-]$ through pOH first, never by guessing the exponent. Write the Ksp expression with the correct exponent on $[OH^-]$ before you substitute any number. And check whether the salt responds to pH at all before you calculate anything.

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

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Section A: Recall and Concepts

A1. (a) State the relationship between pH and pOH at 25 °C. (b) Calculate $[OH^-]$ in a solution of pH 8. (c) State whether raising the pH increases or decreases the solubility of $Mg(OH)_2$, and explain why in one sentence. (d) State what happens to the solubility of AgCl when the pH is lowered from 7 to 3, and explain why.

A2. (a) Write the dissolution equation for $Mg(OH)_2$. (b) Write the Ksp expression for $Mg(OH)_2$. (c) State the exponent on $[OH^-]$ in that expression, and state where the exponent comes from. (d) A student writes $s = Ksp/[OH^-]$ for $Mg(OH)_2$. State the error, and write the correct relationship.

A3. (a) Write the reaction that occurs when F^- meets H^+ in an acidic solution of CaF_2. (b) Explain in one sentence why this reaction increases the solubility of CaF_2. (c) Write the reaction that occurs when CO_3^{2-} meets H^+ in an acidic solution of $CaCO_3$. (d) State what happens to NH_4^+ when OH^- is added, and state whether the solubility of an ammonium salt rises or falls in base.

A4. For each salt, state whether its solubility changes with pH, and give a one-line reason. (a) AgCl. (b) $BaSO_4$. (c) $CaCO_3$. (d) $Fe(OH)_3$. (e) PbI_2. (f) CaF_2.

A5. (a) Define the threshold pH for precipitation of a hydroxide. (b) State the Qsp rule that decides whether a precipitate forms at a stated pH. (c) State what selective precipitation is, in one sentence. (d) State whether Ksp changes when the pH changes, and justify your answer in one sentence.

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Section B: Core Practice

B1. $Mg(OH)_2$ has Ksp = 5.6×10^{-12}. A solution is held at pH 9. (a) Calculate the pOH of the solution. (b) Calculate $[OH^-]$. (c) Calculate the molar solubility s of $Mg(OH)_2$ at this pH. (d) State whether this solubility is larger or smaller than the pure-water solubility of 1.1×10^{-4} M, and give the factor by which they differ. (e) Explain in one sentence why the solubility at pH 9 is so much larger than in pure water.

B2. $Mg(OH)_2$ has Ksp = 5.6×10^{-12}. A solution is held at pH 11. (a) Calculate $[OH^-]$. (b) Calculate the molar solubility s of $Mg(OH)_2$ at this pH. (c) State how many times smaller this solubility is than the pure-water solubility of 1.1×10^{-4} M. (d) Explain in one sentence why the solubility at pH 11 is so much smaller than in pure water. (e) State the factor by which the solubility changes when the pH rises by one unit for $Mg(OH)_2$, and state why the factor is that size.

B3. $Fe(OH)_3$ has Ksp = 2.8×10^{-39}. A solution is held at pH 3. (a) Calculate $[OH^-]$. (b) Calculate the molar solubility s of $Fe(OH)_3$ at this pH. (c) The solubility of $Fe(OH)_3$ at pH 7 is 2.8×10^{-18} M. State the factor by which the solubility rises when the pH falls from 7 to 3. (d) Explain why the factor in part (c) is so large, naming the exponent involved. (e) State whether $Fe(OH)_3$ is appreciably soluble even at pH 3, and justify your answer with the number from part (b).

B4. $Ca(OH)_2$ has Ksp = 5.5×10^{-6}. A solution is held at pH 12. (a) Calculate $[OH^-]$. (b) Calculate the molar solubility s of $Ca(OH)_2$ at this pH. (c) Calculate the molar solubility at pH 13. (d) State the factor by which the solubility falls when the pH rises from 12 to 13. (e) Explain in one sentence why $Ca(OH)_2$ is far more soluble than $Mg(OH)_2$ at the same pH.

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B5. A solution is 0.010 M in Mg^{2+}. $Mg(OH)_2$ has Ksp = 5.6×10^{-12}. (a) Calculate the threshold $[OH^-]$ at which $Mg(OH)_2$ first precipitates. (b) Calculate the pOH at the threshold. (c) Calculate the threshold pH. (d) State whether $Mg(OH)_2$ precipitates if the pH is raised to 10, and justify your answer by comparing pH 10 with the threshold. (e) The Mg^{2+} solution is diluted to 0.0010 M. Calculate the new threshold pH, and state whether dilution raises or lowers the threshold pH.

B6. A solution is 0.020 M in Mg^{2+} and has pH 9.5. $Mg(OH)_2$ has Ksp = 5.6×10^{-12}. (a) Calculate the pOH of the solution. (b) Calculate $[OH^-]$. (c) Calculate Qsp for $Mg(OH)_2$. (d) Compare Qsp with Ksp. (e) State whether $Mg(OH)_2$ precipitates, and explain the verdict in one sentence.

Section C: Exam Style

C1. Judge each claim, supporting each verdict with the definition or the rule it depends on. (a) "Lowering the pH raises the Ksp of $Mg(OH)_2$." (b) "AgCl dissolves more in acid, because acid dissolves every salt." (c) "$Fe(OH)_3$ precipitates from a solution that is 1.0×10^{-4} M in Fe^{3+} at pH 2." (d) "Doubling $[OH^-]$ halves the solubility of $Mg(OH)_2$." (e) "$CaCO_3$ fizzes in acid because CO_3^{2-} is protonated to HCO_3^-."

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C2. A beaker holds a saturated solution of $Mg(OH)_2$ in pure water. Its pH is 10.35 and its solubility is 1.1×10^{-4} M. Acid is added until the pH reaches 10. (a) Calculate $[OH^-]$ at pH 10. (b) Calculate the new molar solubility of $Mg(OH)_2$. (c) State the factor by which the solubility has risen, and state whether the solid in the beaker dissolves further or precipitates. (d) Explain the change in one sentence, using the dissolution equilibrium. (e) Instead of acid, NaOH is added to a fresh saturated solution until the pH reaches 12. Calculate the molar solubility at pH 12, and state whether solid precipitates.

C3. A solution contains Fe^{3+} at 1.0×10^{-4} M and Mg^{2+} at 0.010 M. The pH is raised slowly from 1. $Mg(OH)_2$ has Ksp = 5.6×10^{-12} and $Fe(OH)_3$ has Ksp = 2.8×10^{-39}. (a) Calculate the pH at which $Fe(OH)_3$ first precipitates. (b) Calculate the pH at which $Mg(OH)_2$ first precipitates. (c) State which hydroxide precipitates first, and give the difference between the two threshold pH values. (d) At pH 5, state which metal ions have precipitated and which are still dissolved, justifying each with a Qsp comparison. (e) Explain in one sentence why this procedure separates the two metals.

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Answer Key

A1. (a) pH + pOH = 14 at 25 °C. (b) pOH = 14 − 8 = 6, so $[OH^-] = 1.0 \times 10^{-6}$ M. (c) Raising the pH decreases the solubility: the higher $[OH^-]$ pushes the dissolution equilibrium $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ to the left. (d) It does not change: neither Ag^+ nor Cl^- reacts with H^+ or OH^-, so pH has no effect on AgCl.

A2. (a) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$. (b) $K_{sp} = [Mg^{2+}][OH^-]^2$. (c) The exponent is 2, and it comes from the stoichiometric coefficient of OH^- in the dissolution equation. (d) The error is the missing square: the correct relationship is $s = K_{sp}/[OH^-]^2$.

A3. (a) $F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$. (b) Protonating fluoride removes F^- from the dissolution equilibrium, pulling it to the right so more CaF_2 dissolves. (c) $CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$. (d) NH_4^+ reacts with OH^- to form NH_3 and H_2O, so the solubility of an ammonium salt rises in base.

A4. (a) No change: neither ion reacts with H^+ or OH^-. (b) No change: SO_4^{2-} is the conjugate base of a strong acid. (c) Changes: CO_3^{2-} is protonated in acid, so solubility rises as pH falls. (d) Changes: OH^- is a product of the dissolution, so solubility falls as pH rises. (e) No change: neither Pb^{2+} nor I^- reacts with H^+ or OH^-. (f) Changes: F^- is protonated to HF in acid, so solubility rises as pH falls.

A5. (a) The threshold pH is the pH at which Qsp first reaches Ksp, so solid first appears. (b) Compute Qsp from the current concentrations: if Qsp exceeds Ksp a precipitate forms, if Qsp is below Ksp none forms, if Qsp equals Ksp the solution is saturated. (c) Selective precipitation is raising the pH slowly so that the least soluble hydroxide precipitates first while the others stay dissolved. (d) No: Ksp is an equilibrium constant fixed at a given temperature, and pH changes only the solubility.

B1. (a) pOH = 14 − 9 = 5. (b) $[OH^-] = 1.0 \times 10^{-5}$ M. (c) $s = K_{sp}/[OH^-]^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-5})^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-10}) = 5.6 \times 10^{-2}$ M. (d) Larger: $(5.6 \times 10^{-2})/(1.1 \times 10^{-4}) = 5.1 \times 10^2$, about 510 times larger. (e) pH 9 is more acidic than a saturated solution at pH 10.35, so acid has removed OH^- and pulled the dissolution equilibrium to the right.

B2. (a) pOH = 14 − 11 = 3, so $[OH^-] = 1.0 \times 10^{-3}$ M. (b) $s = K_{sp}/[OH^-]^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-3})^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-6}) = 5.6 \times 10^{-6}$ M. (c) $(1.1 \times 10^{-4})/(5.6 \times 10^{-6}) = 20$, about 20 times smaller. (d) pH 11 is more basic than a saturated solution at pH 10.35, so the extra OH^- pushes the dissolution equilibrium to the left. (e) A factor of one hundred per pH unit, because $[OH^-]$ is squared in the Ksp expression.

B3. (a) pOH = 14 − 3 = 11, so $[OH^-] = 1.0 \times 10^{-11}$ M. (b) $s = K_{sp}/[OH^-]^3 = (2.8 \times 10^{-39})/(1.0 \times 10^{-11})^3 = (2.8 \times 10^{-39})/(1.0 \times 10^{-33}) = 2.8 \times 10^{-6}$ M. (c) $(2.8 \times 10^{-6})/(2.8 \times 10^{-18}) = 1.0 \times 10^{12}$, a factor of a trillion. (d) The exponent on $[OH^-]$ is 3, so each pH unit changes the solubility by a factor of one thousand, and four pH units give $1{,}000^4 = 10^{12}$. (e) No: 2.8×10^{-6} M is still only a few micromoles per litre, so the salt remains barely soluble.

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B4. (a) pOH = 14 − 12 = 2, so $[OH^-] = 1.0 \times 10^{-2}$ M. (b) $s = K_{sp}/[OH^-]^2 = (5.5 \times 10^{-6})/(1.0 \times 10^{-2})^2 = (5.5 \times 10^{-6})/(1.0 \times 10^{-4}) = 5.5 \times 10^{-2}$ M. (c) At pH 13, $[OH^-] = 0.10$ M, so $s = (5.5 \times 10^{-6})/(0.10)^2 = (5.5 \times 10^{-6})/0.010 = 5.5 \times 10^{-4}$ M. (d) $(5.5 \times 10^{-2})/(5.5 \times 10^{-4}) = 100$, a factor of one hundred. (e) Its Ksp is much larger: 5.5×10^{-6} against 5.6×10^{-12} for $Mg(OH)_2$, a factor of about a million.

B5. (a) $[OH^-] = \text{sqrt}(K_{sp}/[Mg^{2+}]) = \text{sqrt}((5.6 \times 10^{-12})/0.010) = \text{sqrt}(5.6 \times 10^{-10}) = 2.4 \times 10^{-5}$ M. (b) $pOH = -\log(2.4 \times 10^{-5}) = 4.63$. (c) pH = 14 − 4.63 = 9.37. (d) Yes: pH 10 is above the threshold pH of 9.37, so Qsp exceeds Ksp and $Mg(OH)_2$ precipitates. (e) $[OH^-] = \text{sqrt}((5.6 \times 10^{-12})/0.0010) = \text{sqrt}(5.6 \times 10^{-9}) = 7.5 \times 10^{-5}$ M, giving pOH = 4.13 and pH = 9.87. Dilution raises the threshold pH, because a more dilute metal solution needs more hydroxide before Qsp reaches Ksp.

B6. (a) pOH = 14 − 9.5 = 4.5. (b) $[OH^-] = 10\text{^}(-4.5) = 3.2 \times 10^{-5}$ M. (c) $Q_{sp} = [Mg^{2+}][OH^-]^2 = (0.020)(3.2 \times 10^{-5})^2 = (0.020)(1.0 \times 10^{-9}) = 2.0 \times 10^{-11}$. (d) $Q_{sp} = 2.0 \times 10^{-11}$ exceeds $K_{sp} = 5.6 \times 10^{-12}$. (e) Yes, $Mg(OH)_2$ precipitates, because Qsp is greater than Ksp, so the solution holds more ions than equilibrium allows.

C1. (a) False. Ksp is fixed at a given temperature; lowering the pH changes the solubility, not Ksp. (b) False. AgCl contains ions from a strong acid and a strong base, so neither ion reacts with H^+ or OH^- and pH has no effect. (c) False. $Fe(OH)_3$ first precipitates from 1.0×10^{-4} M Fe^{3+} at pH 2.48, so at pH 2, below the threshold, no precipitate forms. (d) False. $[OH^-]$ is squared in the Ksp expression for $Mg(OH)_2$, so doubling $[OH^-]$ cuts the solubility by a factor of four, not two. (e) True. CO_3^{2-} is the conjugate base of a weak acid, so H^+ protonates it to HCO_3^-, pulling the dissolution equilibrium to the right and releasing CO_2.

C2. (a) pOH = 14 − 10 = 4, so $[OH^-] = 1.0 \times 10^{-4}$ M. (b) $s = K_{sp}/[OH^-]^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-4})^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-8}) = 5.6 \times 10^{-4}$ M. (c) $(5.6 \times 10^{-4})/(1.1 \times 10^{-4}) = 5.1$, about five times larger, so the solid in the beaker dissolves further. (d) Acid removes OH^- from the solution, so the dissolution equilibrium $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ shifts right to replace it. (e) At pH 12, $[OH^-] = 1.0 \times 10^{-2}$ M, so $s = (5.6 \times 10^{-12})/(1.0 \times 10^{-2})^2 = (5.6 \times 10^{-12})/(1.0 \times 10^{-4}) = 5.6 \times 10^{-8}$ M. The solubility falls far below the pure-water value, so solid precipitates.

C3. (a) $[OH^-] = ((2.8 \times 10^{-39})/(1.0 \times 10^{-4}))\text{^}(1/3) = (2.8 \times 10^{-35})\text{^}(1/3) = 3.0 \times 10^{-12}$ M, giving pOH = 11.52 and pH = 2.48. (b) $[OH^-] = \text{sqrt}((5.6 \times 10^{-12})/0.010) = 2.4 \times 10^{-5}$ M, giving pOH = 4.63 and pH = 9.37. (c) $Fe(OH)_3$ precipitates first: 9.37 − 2.48 = 6.89, about 6.9 pH units earlier. (d) At pH 5, $[OH^-] = 1.0 \times 10^{-9}$ M. For $Fe(OH)_3$, $Q_{sp} = (1.0 \times 10^{-4})(1.0 \times 10^{-9})^3 = 1.0 \times 10^{-31}$, which exceeds $K_{sp} = 2.8 \times 10^{-39}$, so Fe^{3+} has precipitated. For $Mg(OH)_2$, $Q_{sp} = (0.010)(1.0 \times 10^{-9})^2 = 1.0 \times 10^{-20}$, which is below $K_{sp} = 5.6 \times 10^{-12}$, so Mg^{2+} is still dissolved. (e) The two hydroxides have vastly different Ksp values, so their precipitation thresholds are nearly seven pH units apart and one metal can be removed while the other stays in solution.

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