

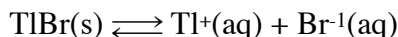
CH 223 Practice Problem Set #4

This is a *practice problem set* and not the actual graded problem set that you will turn in for credit.
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Fifteen** (solubility), **Chapter Sixteen** and **Chapter Guide Four**

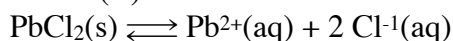
Important Tables and/or Constants: **Solubility Table** (from the CH 221 Net Ionics lab or here: <https://mhchem.org/sol>), **"Solubility Product Constant (K_{sp}) Values at 25 °C"** and **"Complex Ion Formation Constant (K_f) Values at 25 °C"** at the end of problem set #4, **"Solubility Guide"** (Handout), **Table of Thermodynamic Values** (found at the end of CH 223 Problem Set #5 or here: <http://mhchem.org/thermo>)

- Predict whether each of the following is insoluble or soluble in water.
 - $(\text{NH}_4)_2\text{CO}_3$
 - ZnSO_4
 - NiS
 - BaSO_4
- For each of the following insoluble salts, (i) write a balanced equation showing the equilibrium occurring when the salt is added to water and (ii) write the K_{sp} expression.
 - AgCN
 - NiCO_3
 - AuBr_3
- When 1.55 g of solid thallium(I) bromide is added to 1.00 L of water, the salt dissolves to a small extent.



The thallium(I) and bromide ions in equilibrium with TlBr each have a concentration of 1.9×10^{-3} M. What is the value of K_{sp} for TlBr?

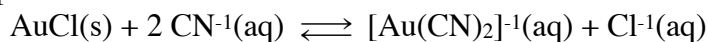
- You add 0.979 g of $\text{Pb}(\text{OH})_2$ to 1.00 L of pure water at 25 °C. The pH is 9.15. Estimate the value of K_{sp} for $\text{Pb}(\text{OH})_2$.
- Estimate the solubility of calcium fluoride, CaF_2 , (a) in moles per liter and (b) in grams per liter of pure water.
$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{F}^-(aq) \quad K_{sp} = 5.3 \times 10^{-11}$$
- The K_{sp} value for radium sulfate, RaSO_4 , is 3.7×10^{-11} . If 25 mg of radium sulfate is placed in 1.00×10^2 mL of water, does all of it dissolve? If not, how much dissolves?
- Use K_{sp} values to decide which compound in each of the following pairs is the more soluble.
 - PbCl_2 ($K_{sp} = 1.7 \times 10^{-5}$) or PbBr_2 ($K_{sp} = 6.6 \times 10^{-6}$)
 - HgS ($K_{sp} = 4.2 \times 10^{-11}$) or FeS ($K_{sp} = 8.0 \times 10^{-19}$)
 - $\text{Fe}(\text{OH})_2$ ($K_{sp} = 4.9 \times 10^{-17}$) or $\text{Zn}(\text{OH})_2$ ($K_{sp} = 3.0 \times 10^{-17}$)
- Compare the solubility, in milligrams per milliliter, of silver iodide, AgI , (a) in pure water and (b) in water that is 0.020 M in AgNO_3 . (K_{sp} for $\text{AgI} = 8.5 \times 10^{-17}$)
- You have a solution that has a lead(II) concentration of 0.0012 M.



If enough soluble chloride-containing salt is added so that the Cl^- concentration is 0.010 M, will PbCl_2 precipitate? (K_{sp} for $\text{PbCl}_2 = 1.7 \times 10^{-5}$)

10. Will a precipitate of $\text{Mg}(\text{OH})_2$ form when 25.0 mL of 0.010 M NaOH is combined with 75.0 mL of a 0.10 M solution of magnesium chloride? (K_{sp} for $\text{Mg}(\text{OH})_2 = 5.6 \times 10^{-12}$)

11. Solid gold(I) chloride, AuCl, dissolves when excess cyanide ion, CN^- , is added to give a water-soluble complex ion.



Show that this equation is the sum of two other equations, one for dissolving AuCl to give its ions ($K_{\text{sp}} = 2.0 \times 10^{-13}$) and the other for the formation of the $[\text{Au}(\text{CN})_2]^{-1}$ ion (using $K_{\text{form}} = 2.0 \times 10^{38}$) from Au^{+1} and CN^- . Calculate K_{net} for the overall reaction.

12. Each pair of ions below is found together in aqueous solution. Using a table of solubility product constants, devise a way to separate these ions by precipitating one of them as an insoluble salt and leaving the other in solution.

- Ba^{2+} and Na^+
- Ni^{2+} and Pb^{2+}

13. A solution contains Ca^{2+} and Pb^{2+} ions, both at a concentration of 0.010 M. You wish to separate the two ions from each other as completely as possible by precipitating one but not the other using aqueous Na_2SO_4 as the precipitating agent.

- Which will precipitate first as sodium sulfate is added, CaSO_4 or PbSO_4 ?
- What will be the concentration of the first ion that precipitates (Ca^{2+} or Pb^{2+}) when the second, more soluble salt begins to precipitate?

14. Explain why the solubility of Ag_3PO_4 can be greater in water than is calculated from the K_{sp} value of the salt.

15. Which substance has the higher entropy in each of the following pairs?

- dry ice (solid CO_2) at -78°C or $\text{CO}_2(\text{g})$ at 0°C
- liquid water at 25°C or liquid water at 50°C
- pure alumina, $\text{Al}_2\text{O}_3(\text{s})$, or ruby (ruby is $\text{Al}_2\text{O}_3(\text{s})$ in which some of the Al^{3+} ions in the crystalline lattice are replaced with Cr^{3+} ions.)
- one mole of $\text{N}_2(\text{g})$ at 1 bar pressure or one mole of $\text{N}_2(\text{g})$ at 10 bar pressure (both at 298 K)

16. By comparing the formulas for each pair of compounds, decide which is expected to have the higher entropy. Assume all are at the same temperature.

- $\text{O}_2(\text{g})$ or $\text{CH}_3\text{OH}(\text{g})$ (two substances with the same molar mass)
- $\text{HF}(\text{g})$, $\text{HCl}(\text{g})$, or $\text{HBr}(\text{g})$
- $\text{NH}_4\text{Cl}(\text{s})$ or $\text{NH}_4\text{Cl}(\text{aq})$
- $\text{HNO}_3(\text{g})$, $\text{HNO}_3(\text{l})$, or $\text{HNO}_3(\text{aq})$

17. Use S° values to calculate the entropy change, ΔS° , for each of the following processes and comment on the sign of the change.

- $\text{LiOH}(\text{s}) \rightarrow \text{LiOH}(\text{aq})$ (Note: $S^\circ(\text{LiOH}(\text{aq})) = 91.6 \text{ J/molK}$)
- $\text{Na}(\text{g}) \rightarrow \text{Na}(\text{s})$
- $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
- $\text{HCl}(\text{g}) \rightarrow \text{HCl}(\text{aq})$ (Note: $S^\circ(\text{HCl}(\text{aq})) = 56.5 \text{ J/molK}$)

18. Calculate the standard molar entropy change of formation (ΔS_f°) for each of the following compounds from the elements at 25°C .

- $\text{HCl}(\text{g})$
- $\text{Ca}(\text{OH})_2(\text{s})$

19. Calculate the standard molar entropy change for each of the following reactions at 25°C . Comment on the sign of ΔS° .

- a. $2 \text{Al(s)} + 3 \text{Cl}_2\text{(g)} \rightarrow 2 \text{AlCl}_3\text{(s)}$
b. $2 \text{CH}_3\text{OH(l)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)} + 4 \text{H}_2\text{O(g)}$

Answers to the Practice Problem Set:

- (a) and (b): soluble, (c) and (d): insoluble
- Answers:
 - $\text{AgCN}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{CN}^-(aq) \quad K_{sp} = [\text{Ag}^+][\text{CN}^-]$
 - $\text{NiCO}_3(s) \rightleftharpoons \text{Ni}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K_{sp} = [\text{Ni}^{2+}][\text{CO}_3^{2-}]$
 - $\text{AuBr}_3(s) \rightleftharpoons \text{Au}^{3+}(aq) + 3 \text{Br}^-(aq) \quad K_{sp} = [\text{Au}^{3+}][\text{Br}^-]^3$
- 3.6×10^{-6}
- 1.4×10^{-15}
- a. 2.4×10^{-4} b. 0.018
- No; 0.20 mg dissolves
- a. PbCl_2 b. HgS b. $\text{Fe}(\text{OH})_2$
- a. 2.2×10^{-6} b. 1.0×10^{-13}
- $Q < K_{sp}$ so no precipitate
- $Q > K_{sp}$ so precipitate forms
- $K_{net} = 4.0 \times 10^{25}$
- a. SO_4^{2-} will precipitate Ba^{2+} b. Cl^- will precipitate Pb^{2+}
- a. PbSO_4 b. $5.1 \times 10^{-6} \text{ M}$
- PO_4^{3-} acts as a base, increasing solubility upon formation of HPO_4^{2-}
- a. $\text{CO}_2(g)$ b. $50^\circ \text{H}_2\text{O}(l)$ c. ruby d. $\text{N}_2(g)$ at 1 bar
- a. $\text{CH}_3\text{OH}(g)$ b. $\text{HBr}(g)$ c. $\text{NH}_4\text{Cl}(aq)$ d. $\text{HNO}_3(g)$
- a. 48.8 J/K (entropy increase) b. -102.4 J/K (entropy decrease) c. 93.3 J/K (entropy increase) d. -130.4 J/K (entropy decrease) (*Instructor note: your values of ΔS might be slightly different depending on the textbook used, etc., but they should be close to these values.*)
- a. 10.0 J/K b. -294.1 J/K (see note in answer #17, above)
- a. -504.6 J/K (entropy increase) b. 313.6 J/K (entropy decrease) (see note in answer #17, above)