

CH 223 Spring 2024:

Problem Set #4

Instructions

Step One (all sections):

- **Learn the material** for Problem Set #4 by **reading Chapter 15 and Chapter 16** of the textbook and/or by watching the videos found on our website (<https://mhchem.org/223>)
- **Try the problems** for Problem Set #4 found on the next pages on your own first. Use separate paper and write out your answers, showing all of your work. If you write the answers on the problem set itself, you will receive fewer points. Include your name on your problem set!

Step Two:

Section 01 and H1: We will go over Problem Set #4 during recitation. ***Self correct all problems*** of your problem set before turning it in at the end of recitation.

- *Section 01:* due **Monday, May 13 at 1:10 PM**
- *Section H1:* due **Wednesday, May 15 at 1:10 PM**

Section W1: **Watch the recitation video** for Problem Set #4:

<http://mhchem.org/v/r.htm>

- **Self correct all of the problems** while viewing the video. Mark correct problems with a star (or other similar mark), and correct all incorrect problems (show the correct answer and the steps required to achieve it.)
- **Submit Problem Set #4 via email (mike.russell@mhcc.edu) as a single PDF file** (use CamScanner (<https://camscanner.com>), CombinePDF (<https://combinepdf.com>), etc.) by **11:59 PM Wednesday, May 15.**

If you have any questions regarding this assignment, please email (mike.russell@mhcc.edu) the instructor! Good luck on this assignment!

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* Complete problem set on separate pieces of paper showing all work, circling final answers, etc.

* Self correct your work before turning it in to the instructor.

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>)

- Using a solubility table, predict whether the following are insoluble or soluble in water.
 - $\text{Pb}(\text{NO}_3)_2$
 - $\text{Fe}(\text{OH})_3$
 - ZnCl_2
 - CuS
- For PbSO_4 and BaF_2 , (i) write a balanced equation showing the equilibrium occurring when each insoluble salt is added separately to water, and (ii) write the K_{sp} expression.
 - Write a balanced equation showing the equilibrium occurring for the formation of the complex ion $\text{Zn}(\text{NH}_3)_4^{2+}(\text{aq})$ and write the corresponding K_f expression.
- At 20 °C, a saturated aqueous solution of silver(I) acetate, AgCH_3CO_2 , contains 0.74 g of the silver compound dissolved in 100.0 mL of solution. Calculate K_{sp} for silver(I) acetate.
$$\text{AgCH}_3\text{CO}_2(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$$
- What is the molar concentration of $\text{Au}^+(\text{aq})$ in a saturated solution of AuCl ($K_{sp} = 2.0 \times 10^{-13}$) in pure water at 25 °C? The equation:
$$\text{AuCl}(\text{s}) \rightleftharpoons \text{Au}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
- Estimate the solubility of lead(II) bromide (a) in moles per liter and (b) in grams per liter of pure water. (K_{sp} for lead(II) bromide = 6.6×10^{-6})
- If 75 mg of lead(II) sulfate is placed in 250 mL of pure water, does all of it dissolve? If not, how much dissolves? (K_{sp} for lead(II) sulfate = 2.5×10^{-8})
- You place 2.234 g of solid $\text{Ca}(\text{OH})_2$ in 1.00 L of pure water at 25 °C. The pH of the solution is found to be 12.68. Estimate the K_{sp} for $\text{Ca}(\text{OH})_2$.
- Which compound in each of the following pairs is the more soluble?
 - AgBr ($K_{sp} = 5.0 \times 10^{-13}$) or AgSCN ($K_{sp} = 1.0 \times 10^{-12}$)
 - SrCO_3 ($K_{sp} = 9.3 \times 10^{-10}$) or SrSO_4 ($K_{sp} = 3.4 \times 10^{-7}$)
 - AgI ($K_{sp} = 8.3 \times 10^{-17}$) or PbI_2 ($K_{sp} = 9.8 \times 10^{-9}$)
- What is the solubility, in milligrams per milliliter, of BaF_2 (a) in pure water, and (b) in water containing 5.0 mg/mL KF? (K_{sp} for $\text{BaF}_2 = 1.8 \times 10^{-7}$)
- Sodium carbonate is added to a solution in which the concentration of Ni^{2+} ion is 0.0024 M. Will precipitation of NiCO_3 ($K_{sp} = 1.4 \times 10^{-7}$) occur (a) when the concentration of the carbonate ion is 1.0×10^{-6} M or (b) when it is 100 times greater (or 1.0×10^{-4} M)? The equation:
$$\text{NiCO}_3(\text{s}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$
- You have 95 mL of a solution that has a lead(II) concentration of 0.0012 M. Will PbCl_2 precipitate when 1.20 g of solid NaCl is added? (K_{sp} for $\text{PbCl}_2 = 1.7 \times 10^{-5}$)

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12. Solid silver(I) iodide, AgI, can be dissolved by adding aqueous sodium cyanide to it (see equation below.) Show that this equation is the sum of two other equations, one for dissolving AgI ($K_{sp} = 8.3 \times 10^{-17}$) to give its ions and the other for the formation of the $[\text{Ag}(\text{CN})_2]^{-1}$ ion ($K_f = 1.3 \times 10^{21}$) from Ag^+ and CN^{-1} . Calculate K_{net} for the overall reaction. The equation:
- $$\text{AgI}(\text{s}) + 2 \text{CN}^{-1}(\text{aq}) \rightleftharpoons [\text{Ag}(\text{CN})_2]^{-1}(\text{aq}) + \text{I}^{-1}(\text{aq})$$
13. You have a solution with aqueous Cu^{2+} and Ag^+ ions. Using a table of solubility product constants, devise a way to separate these ions by adding one reagent to precipitate one of them as an insoluble salt and leave the other in solution.
14. A solution contains 0.10 M iodide ion, I^{-1} , and 0.10 M carbonate ion, CO_3^{2-} .
- If solid $\text{Pb}(\text{NO}_3)_2$ is slowly added to the solution, which salt will precipitate first, PbI_2 or PbCO_3 ? (K_{sp} for $\text{PbI}_2 = 9.8 \times 10^{-9}$, K_{sp} for $\text{PbCO}_3 = 7.4 \times 10^{-14}$)
 - What will be the concentration of the first ion that precipitates (CO_3^{2-} or I^{-1}) when the second, more soluble salt begins to precipitate?
15. Which substance has the higher entropy in each of the following pairs?
- a sample of pure silicon (to be used in a computer chip) or a piece of silicon containing traces of other elements such as boron or phosphorus
 - $\text{O}_2(\text{g})$ at 0°C or $\text{O}_2(\text{g})$ at -50°C
 - $\text{I}_2(\text{s})$ or $\text{I}_2(\text{g})$, both at room temperature
 - $\text{C}_2\text{H}_4(\text{g})$ or $\text{N}_2(\text{g})$ (two substances with the same molar mass)
16. Using a table of S° values, calculate the entropy change, ΔS° , for each of the following changes and comment on the sign of the change.
- $\text{C}_2\text{H}_5\text{OH}(\ell) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
 - $\text{CCl}_4(\text{g}) \rightarrow \text{CCl}_4(\ell)$
17. Calculate the standard molar entropy change of formation (ΔS_f°) for each of the following compounds from the elements at 25°C .
- $\text{H}_2\text{S}(\text{g})$ (Note: sulfur is an octamer (S_8))
 - $\text{Li}_2\text{CO}_3(\text{s})$

Solubility Product Constant (K_{sp}) Values at 25 °C

Formation Equilibrium	K
$\text{Ag}^+ + 2 \text{Br}^- \rightleftharpoons [\text{AgBr}_2]^-$	2.1×10^7
$\text{Ag}^+ + 2 \text{Cl}^- \rightleftharpoons [\text{AgCl}_2]^-$	1.1×10^5
$\text{Ag}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$	1.3×10^{21}
$\text{Ag}^+ + 2 \text{S}_2\text{O}_3^{2-} \rightleftharpoons [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	2.9×10^{13}
$\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$	1.1×10^7
$\text{Al}^{3+} + 6 \text{F}^- \rightleftharpoons [\text{AlF}_6]^{3-}$	6.9×10^{19}
$\text{Al}^{3+} + 4 \text{OH}^- \rightleftharpoons [\text{Al}(\text{OH})_4]^-$	1.1×10^{33}
$\text{Au}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Au}(\text{CN})_2]^-$	2.0×10^{38}
$\text{Cd}^{2+} + 4 \text{CN}^- \rightleftharpoons [\text{Cd}(\text{CN})_4]^{2-}$	6.0×10^{18}
$\text{Cd}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Cd}(\text{NH}_3)_4]^{2+}$	1.3×10^7
$\text{Co}^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+}$	1.3×10^5
$\text{Cu}^+ + 2 \text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_2]^-$	1.0×10^{24}
$\text{Cu}^+ + 2 \text{Cl}^- \rightleftharpoons [\text{CuCl}_2]^-$	3.2×10^5
$\text{Cu}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$	2.1×10^{13}
$\text{Fe}^{2+} + 6 \text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	1.0×10^{35}
$\text{Hg}^{2+} + 4 \text{Cl}^- \rightleftharpoons [\text{HgCl}_4]^{2-}$	1.2×10^{15}
$\text{Ni}^{2+} + 4 \text{CN}^- \rightleftharpoons [\text{Ni}(\text{CN})_4]^{2-}$	2.0×10^{31}
$\text{Ni}^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$	5.5×10^8
$\text{Zn}^{2+} + 4 \text{OH}^- \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}$	4.6×10^{17}
$\text{Zn}^{2+} + 4 \text{NH}_3 \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+}$	2.9×10^9

*Data reported in this table are taken from J. A. Dean: *Lange's Handbook of Chemistry*, 15th ed. New York: McGraw-Hill Publishers, 1999.

Complex Ion Formation Constant (K_f) Values at 25 °C

Cation	Compound	K_{sp}	Cation	Compound	K_{sp}			
Ba ²⁺	*BaCrO ₄	1.2×10^{-10}	Hg ₂ ²⁺	*Hg ₂ Br ₂	6.4×10^{-23}			
	BaCO ₃	2.6×10^{-9}		Hg ₂ Cl ₂	1.4×10^{-18}			
	BaF ₂	1.8×10^{-7}		*Hg ₂ I ₂	2.9×10^{-29}			
	*BaSO ₄	1.1×10^{-10}		Hg ₂ SO ₄	6.5×10^{-7}			
Ca ²⁺	CaCO ₃ (calcite)	3.4×10^{-9}	Ni ²⁺	NiCO ₃	1.4×10^{-7}			
	*CaF ₂	5.3×10^{-11}		Ni(OH) ₂	5.5×10^{-16}			
	*Ca(OH) ₂	5.5×10^{-5}	Ag ⁺	*AgBr	5.4×10^{-13}			
	CaSO ₄	4.9×10^{-5}		*AgBrO ₃	5.4×10^{-5}			
Cu ⁺ , Cu ²⁺	CuBr	6.3×10^{-9}		AgCH ₃ CO ₂	1.9×10^{-3}			
	CuI	1.3×10^{-12}		AgCN	6.0×10^{-17}			
	Cu(OH) ₂	2.2×10^{-20}	Ag ₂ CO ₃	8.5×10^{-12}				
	CuSCN	1.8×10^{-13}	*Ag ₂ C ₂ O ₄	5.4×10^{-12}				
Au ⁺	AuCl	2.0×10^{-13}	*AgCl	1.8×10^{-10}				
	Fe ²⁺	FeCO ₃	3.1×10^{-11}	Ag ₂ CrO ₄	1.1×10^{-12}			
Fe(OH) ₂		4.9×10^{-17}	*AgI	8.5×10^{-17}				
Pb ²⁺	PbBr ₂ PbCO ₃ PbCl ₂ PbCrO ₄ PbF ₂ PbI ₂ Pb(OH) ₂ PbSO ₄	6.6×10^{-6} 7.4×10^{-14} 1.7×10^{-5} 2.8×10^{-13} 3.3×10^{-8} 9.8×10^{-9} 1.4×10^{-15} 2.5×10^{-8}	Sr ²⁺	SrCO ₃	5.6×10^{-10}			
				SrF ₂	4.3×10^{-9}			
				SrSO ₄	3.4×10^{-7}			
			Tl ⁺	TlBr	3.7×10^{-6}			
				TlCl	1.9×10^{-4}			
				TlI	5.5×10^{-8}			
			Mg ²⁺	MgCO ₃	6.8×10^{-6}	Zn ²⁺	Zn(OH) ₂	3×10^{-17}
				MgF ₂	5.2×10^{-11}		Zn(CN) ₂	8.0×10^{-12}
Mg(OH) ₂	5.6×10^{-12}	Mn ²⁺		MnCO ₃	2.3×10^{-11}			
*Mn(OH) ₂	1.9×10^{-13}							

The values reported in this table were taken from J. A. Dean: *Lange's Handbook of Chemistry*, 15th ed. New York: McGraw-Hill Publishers, 1999. Values have been rounded off to two significant figures.

*Calculated solubility from these K_{sp} values will match experimental solubility for this compound within a factor of 2. Experimental values for solubilities are given in R. W. Clark and J. M. Bonicamp: *Journal of Chemical Education*, Vol. 75, p. 1182, 1998.

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