

HOMEWORK #3

- 11.32 (a) Assume that neither the Mg^{2+} ion nor the OH^- ion from the dissolution of the $\text{Mg}(\text{OH})_2$ interacts further in the solution. Then, if S is the solubility of the $\text{Mg}(\text{OH})_2$, the concentration of Mg^{2+} ion is S and the concentration of OH^- ion is $2S$. At equilibrium,

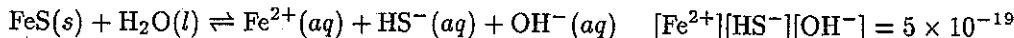
$$K_{\text{sp}} = 1.2 \times 10^{-11} = S(2S)^2 \quad \text{from which} \quad S = 1.4 \times 10^{-4} \text{ mol L}^{-1}$$

(b) If the pH is buffered at a value of 9, then the $[\text{OH}^-]$ is being held at 10^{-5} M. This concentration is *less* than what forms from the dissolution of the $\text{Mg}(\text{OH})_2$ in pure water. After the dissolution of $\text{Mg}(\text{OH})_2$ comes to equilibrium, the concentration of OH^- ion remains at 10^{-5} M because of the action of the buffer. Let S again represent the solubility of the salt. Then:

$$K_{\text{sp}} = 1.2 \times 10^{-11} = S(10^{-5})^2$$

and the solubility is 0.12 mol L^{-1} .

- 11.41 Precipitation of $\text{FeS}(s)$ can begin only if the pH is high enough to make the reaction quotient Q for the reaction:



exceed the K .⁵ Compute the $[\text{H}_3\text{O}^+]$ that barely causes $\text{FeS}(s)$ to precipitate. This concentration is reached when the following equation (obtained as in 11.39) is satisfied:

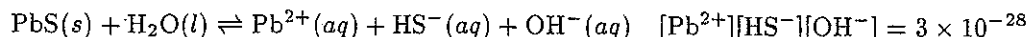
$$[\text{Fe}^{2+}] \left(\frac{K_{\text{a1}}[\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]} \right) \left(\frac{K_{\text{w}}}{[\text{H}_3\text{O}^+]} \right) = 5 \times 10^{-19}$$

Solve for $[\text{H}_3\text{O}^+]$ and substitute the various numbers. The K_{a1} of H_2S equals 9.1×10^{-8} ; K_{w} equals 1.0×10^{-14} ; the concentration of H_2S is 0.10 M; the concentration of Fe^{2+} is 0.10 M:

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{\frac{[\text{Fe}^{2+}]K_{\text{a1}}[\text{H}_2\text{S}]K_{\text{w}}}{5 \times 10^{-19}}} \\ &= \sqrt{\frac{(0.10)(9.1 \times 10^{-8})(0.10)(1.0 \times 10^{-14})}{5 \times 10^{-19}}} = 4.3 \times 10^{-3} \text{ M} \end{aligned}$$

This is the minimum concentration of H_3O^+ that keeps FeS in solution. The maximum pH is therefore 2.4. Higher pH, (implying lower $[\text{H}_3\text{O}^+]$ and higher $[\text{OH}^-]$) shifts the dissolution reaction to the left, causing a precipitate.

The dissolution of $\text{PbS}(s)$ is similar to that of $\text{FeS}(s)$:



and the expression:

$$[\text{Pb}^{2+}] \left(\frac{K_{\text{a1}}[\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]} \right) \left(\frac{K_{\text{w}}}{[\text{H}_3\text{O}^+]} \right) = 3 \times 10^{-28}$$

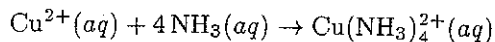
is therefore easily written. Substitution of 0.10 for $[\text{H}_2\text{S}]$, 4.3×10^{-3} for $[\text{H}_3\text{O}^+]$, and 9.1×10^{-8} for K_{a1} gives $[\text{Pb}^{2+}]$ equal to $6 \times 10^{-11} \text{ M}$, which is very small.

Tip. The point is that at pH 2.4, all the Fe^{2+} but (essentially) none of the Pb^{2+} stays in solution.

⁴See text Table 11.4, text page 378.

⁵The K 's in this problem come from text Table 11.3.

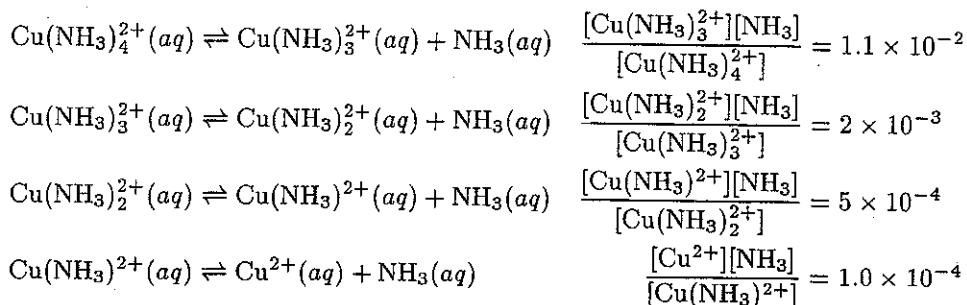
11.43 The copper(II) nitrate dissolves readily to give $\text{Cu}^{2+}(\text{aq})$ and NO_3^- ions. Imagine that the $\text{Cu}^{2+}(\text{aq})$ reacts to completion with the $\text{NH}_3(\text{aq})$ (which is in excess) to form $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$:



Then:

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 0.10 \text{ M} \quad \text{and} \quad [\text{NH}_3] = 1.50 - 4(0.10) = 1.10 \text{ M}$$

Now, imagine free Cu^{2+} ion to come from back-reaction (dissociation of $\text{Cu}(\text{NH}_3)_4^{2+}$). The back-reaction, or dissociation, would proceed in four steps:



where the four constants equal the reciprocals of K_4 through K_1 in text Table 11.4.⁶ Label the concentrations of the four Cu-containing products x , y , z , and w respectively, and calculate them in turn. Treat the steps as if they occurred independently. That is, neglect the amount of Cu-containing product reacted away by later steps and assume that NH_3 from later steps adds only negligibly to the 1.10 M NH_3 present when dissociation starts. For the first step:

	$\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$	\rightleftharpoons	$\text{Cu}(\text{NH}_3)_3^{2+}(\text{aq})$	+	$\text{NH}_3(\text{aq})$
Init. Conc. (mol L ⁻¹)	0.10		0		1.1
Change in Conc. (mol L ⁻¹)	- x		+ x		+ x
Equil. Conc. (mol L ⁻¹)	0.10 - x		x		1.1 + x

$$\frac{[\text{Cu}(\text{NH}_3)_3^{2+}][\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = 1.1 \times 10^{-2} = \frac{x(1.1 + x)}{0.10 - x} \quad \text{which gives} \quad x = 9.9 \times 10^{-4}$$

The set-up for the second step is similar. It gives

$$\frac{[\text{Cu}(\text{NH}_3)_2^{2+}][\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_3^{2+}]} = 2 \times 10^{-3} = \frac{y(1.1 + y)}{9.9 \times 10^{-4} - y} \quad \text{from which:} \quad y = 1.8 \times 10^{-6}$$

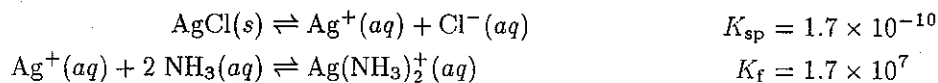
For the third step:

$$\frac{[\text{Cu}(\text{NH}_3)^{2+}][\text{NH}_3]}{[\text{Cu}(\text{NH}_3)_2^{2+}]} = 5 \times 10^{-4} = \frac{z(1.1 + z)}{1.8 \times 10^{-6} - z} \quad \text{which gives} \quad z = 8.2 \times 10^{-10}$$

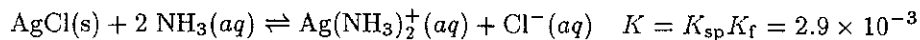
For the fourth step:

$$\frac{[\text{Cu}^{2+}][\text{NH}_3]}{[\text{Cu}(\text{NH}_3)^{2+}]} = 1.0 \times 10^{-4} = \frac{w(1.1 + w)}{8.2 \times 10^{-10} - w} \quad \text{which gives} \quad w = 7.4 \times 10^{-14}$$

⁶See text page 380. The product of K_1 through K_4 equals 0.9×10^{12} , but K_f equals 1.1×10^{12} in the table. This inconsistency arises from rounding off the step-wise K 's and is unimportant.



Adding the second equation to the first gives



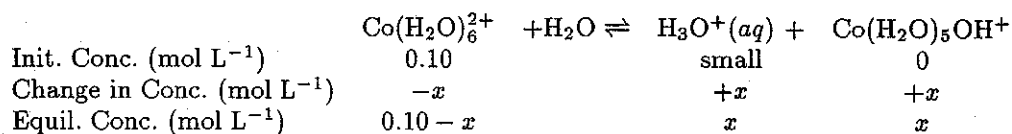
$$[\text{NH}_3] = 1.0 - 2x \quad \text{and} \quad [\text{Ag}(\text{NH}_3)_2^+] = x = [\text{Cl}^-]$$

$$\frac{x^2}{(1.0 - 2x)^2} = 2.9 \times 10^{-3}$$

$$\frac{x}{1.0 - 2x} = 0.054 \quad \text{so that} \quad x = 0.049 = [\text{Ag}(\text{NH}_3)_2^+]$$

0.049 mol AgCl dissolves per liter, or (0.049 mol)(143.3 g mol⁻¹) = 7.0 g.

11.51 The computation is like other computations of the pH of solutions of weak acids.⁸ The coordinated cobalt(II) ion is acidic:

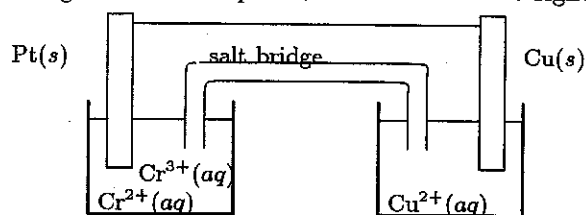


The equilibrium expression is

$$\frac{[\text{H}_3\text{O}^+][\text{Co}(\text{H}_2\text{O})_5\text{OH}^+]}{[\text{Co}(\text{H}_2\text{O})_6^{2+}]} = K_{\text{a}} = 3 \times 10^{-10} = \frac{x^2}{0.10 - x}$$

Solve the equation to obtain $x = 5.5 \times 10^{-6}$. The concentration of H_3O^+ is 5.5×10^{-6} M, and the pH is therefore 5.3.

12.1 Electrons flow from the left electrode to the right as Cr(II) is oxidized to Cr(III). In the salt bridge, negative ions flow from right to left and positive ions from left to right.



12.3 Formation of 1 mol of Sn(s) from Sn⁴⁺(aq) ions requires 4 mol of electrons: Sn⁴⁺(aq) + 4e⁻ → Sn(s). Hence:

$$N_{\text{Sn}} = 6.95 \times 10^4 \text{ C} \times \left(\frac{1 \text{ mol } e^-}{96485.3 \text{ C}} \right) \times \left(\frac{1 \text{ mol Sn}}{4 \text{ mol } e^-} \right) = \boxed{0.180 \text{ mol Sn}}$$

Tip. Note the careful use of the word “maximum” in the statement of the problem. No Sn(s) is necessarily formed by the passage of the current because other electrolytic processes could take place to carry the current.

12.7 Calculate the ratio of the chemical amounts of oxygen and copper generated by the operation of the cell. The molar mass of oxygen is 32.0 g mol⁻¹, and the molar mass of copper is 63.54 g mol⁻¹. The cell therefore forms 0.500 mol of O₂ as it forms 1.00 mol of Cu. A balanced half-equation for the oxidation of water to gaseous oxygen is 3H₂O(l) → 1/2O₂(g) + 2H₃O⁺(aq) + 2e⁻. This equation states that the production of 1/2 mol of O₂ releases 2 mol of electrons. Hence:

$$\frac{0.500 \text{ mol O}_2}{1.00 \text{ mol Cu}} \times \left(\frac{2 \text{ mol } e^-}{1/2 \text{ mol O}_2} \right) = \frac{2.00 \text{ mol } e^-}{1 \text{ mol Cu}}$$

The copper starts off in the +2 oxidation state and is reduced as follows: Cu²⁺(aq) + 2e⁻ → Cu(s).

12.8 Multiplying the relative mass of hydrogen liberated by 1 gives close to the known atomic weight of H. Similarly multiplying the given relative mass by 2 for oxygen, by 1 for chlorine and by 2 for tin gives close to the respective relative atomic masses of the elements. The absolute values of the oxidation states of the four elements (hydrogen, oxygen, chlorine, and tin) are therefore in the ratio 1 to 2 to 1 to 2. This follows from Faraday’s law that a given

amount of charge liberates different substances in proportion to their molar masses (atomic masses) divided by the absolute values of their oxidation numbers.

The hydrogen is liberated at the cathode and must come from the reduction of +1 hydrogen (H⁺); other positive oxidation states of hydrogen are nearly unknown. The oxygen is liberated at the *anode*, and so the oxidation state of the oxygen is -2. The oxidation state for chlorine is -1 and that for tin is +2.