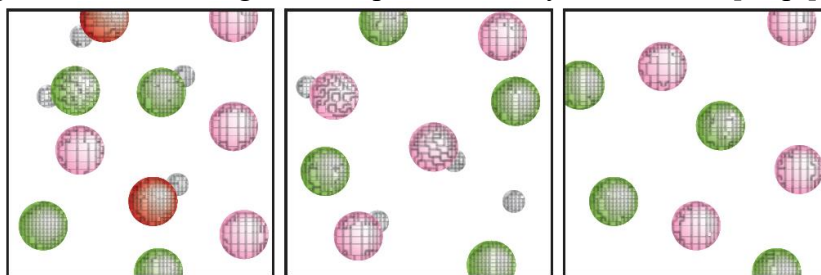


## 2023 Fall Chemistry 2

### Assignment 2 (Atkins, Focus 6)

(Total 200 pt; Due 2023/11/1 Class)

1. The images below represent the solutes in the solutions of three salts (water molecules are not shown, hydrogen atoms and hydronium ions are represented by small gray spheres, hydroxide ions by red and gray spheres, cations by pink spheres, and anions by green spheres). (a) Which salt has a cation that is the conjugate acid of a weak base? (b) Which salt has an anion that is the conjugate base of a weak acid? (c) Which salt has an anion that is the conjugate base of a strong acid? Explain each of your answers. [15 pt]

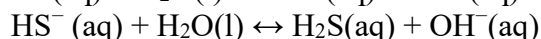
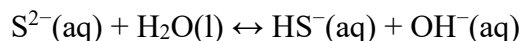


(1)

(2)

(3)

2. Many reactions that take place in water have analogous reactions in liquid ammonia (normal boiling point,  $-33\text{ }^{\circ}\text{C}$ ). (a) Write the chemical equation for the autoprotolysis of  $\text{NH}_3$ . (b) Write the formulas of the acid and base species that result from the autoprotolysis of liquid ammonia. (c) The autoprotolysis constant,  $K_{\text{am}}$ , of liquid ammonia has the value  $1 \times 10^{-33}$  at  $-35\text{ }^{\circ}\text{C}$ . What is the value of  $\text{p}K_{\text{am}}$  at that temperature? (d) What is the molar concentration of  $\text{NH}_4^+$  ions in liquid ammonia? (e) Evaluate  $\text{pNH}_4$  and  $\text{pNH}_2$ , which are the analogs of pH and pOH, in liquid ammonia at  $-35\text{ }^{\circ}\text{C}$ . (f) Derive the relation between  $\text{pNH}_4$ ,  $\text{pNH}_2$ , and  $\text{p}K_{\text{am}}$ . [30 pt]
3. The Topic 6C discusses the relationship between molecular structure and the strengths of acids. The same ideas can be applied to bases. (a) Explain the relative strengths of the Brønsted bases  $\text{OH}^-$ ,  $\text{NH}_2^-$ , and  $\text{CH}_3^-$  (see Table 6C.3). (b) Explain why  $\text{NH}_3$  is a weak base in water, but  $\text{PH}_3$  forms essentially neutral solutions. (c) If you were ranking the species in (a) or (b) as Lewis bases, would your rankings be the same or different? Explain your reasoning. [15 pt]
4. You require 0.150 L of a buffer solution with  $\text{pH} = 3.00$ . On the shelf is a bottle of trichloroacetic acid/sodium trichloroacetate buffer with  $\text{pH} = 2.95$ . The label also says  $[\text{trichloroacetate ion}] = 0.200\text{ mol} \cdot \text{L}^{-1}$ . What mass of which substance (trichloroacetic acid or sodium trichloroacetate) should you add to 0.150 L of the buffer to obtain the desired pH? [10 pt]
5. A sample of 0.150 M  $\text{Na}_2\text{CO}_3(\text{aq})$  of volume 25.0 mL is titrated with 0.100 M  $\text{HCl}(\text{aq})$ . What is the pH of the solution at each stoichiometric point in the titration? [10 pt]
6. Consider the equilibria  
$$\text{ZnS}(\text{s}) \leftrightarrow \text{Zn}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$$



- (a) Write the chemical equation for the overall equilibrium and determine the corresponding equilibrium constant. (b) Evaluate the solubility of ZnS in a saturated  $\text{H}_2\text{S}$  solution, 0.1 M  $\text{H}_2\text{S}(\text{aq})$ , adjusted to  $\text{pH} = 7.0$ . (c) Evaluate the solubility of ZnS in a saturated  $\text{H}_2\text{S}$  solution, 0.1 M  $\text{H}_2\text{S}(\text{aq})$ , adjusted to  $\text{pH} = 10.0$ . [15 pt]
7. The pH of the blood is maintained by a buffering system consisting primarily of hydrogen carbonate ion ( $\text{HCO}_3^{-}$ ) and  $\text{H}_3\text{O}^{+}$  in equilibrium with water and  $\text{CO}_2$ :  

$$\text{H}_3\text{O}^{+}(\text{aq}) + \text{HCO}_3^{-}(\text{aq}) \leftrightarrow 2\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$
During exercise,  $\text{CO}_2$  is produced at a rapid rate in muscle tissue. (a) How does exercise affect the pH of blood? (b) Hyperventilation (rapid and deep breathing) can occur during intense exertion. How does hyperventilation affect the pH of the blood? (c) The normal first-aid treatment for hyperventilation is to have the patient breathe into a paper bag. Explain briefly why this treatment works and tell what effect the paper-bag treatment has on the pH of the blood. See Box 6G.1. [15 pt]
8. State how the oxidizing strength of each of the following oxidizing agents would be affected by raising the pH (stronger, weaker, or no change): (a)  $\text{Br}_2$ ; (b)  $\text{MnO}_4^{-}$ ; (c)  $\text{NO}_3^{-}$ ; (d)  $\text{ClO}_4^{-}$ ; (e)  $\text{Cu}^{2+}$ . Justify your answers. [25 pt]
9. Using data in Appendix 2B, calculate the standard potential for the half-reaction  $\text{Ti}^{4+}(\text{aq}) + 4\text{e}^{-} \rightarrow \text{Ti}(\text{s})$ . [15 pt]
10. Cyclohexane Suppose that 35.0 mL of 0.012 M  $\text{Cu}^{+}(\text{aq})$  is titrated with 0.010 M  $\text{KBr}(\text{aq})$  at 25 °C. A copper electrode is immersed in this solution, and its potential is measured relative to a standard hydrogen electrode. What volume of the  $\text{KBr}$  solution must be added to reach the stoichiometric point, and what will the potential be at that point?  $K_{\text{sp}}(\text{CuBr}) = 5.2 \times 10^{-9}$ . [15 pt]
11. (a) What is the standard cell potential ( $E_{\text{cell}}^{\circ}$ ) for the reaction below at 298 K? (b) What is the standard cell potential for the reaction at 335 K? (c) What is the cell potential for the reaction at 335 K when  $[\text{Zn}^{2+}] = 2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  and  $[\text{Pb}^{2+}] = 1.0 \text{ mol} \cdot \text{L}^{-1}$  (See Exercise 6.59.)  

$$\text{Pb}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Pb}(\text{s})$$
[15 pt]
12. The entropy change of a cell reaction can be determined from the change of the cell potential with temperature. (a) Show that  $\Delta S^{\circ} = nF(E_{\text{cell},2}^{\circ} - E_{\text{cell},1}^{\circ}) / (T_2 - T_1)$ . Assume that  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$  are constant over the temperature range considered. (b) Calculate  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$  for the cell reaction  $\text{Hg}_2\text{Cl}_2(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{Hg}(\text{l}) + 2\text{H}^{+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ , given that  $E^{\circ} = +0.2699 \text{ V}$  at 293 K and  $+0.2669 \text{ V}$  at 303 K. [20 pt]