

2019 Spring Semester Quiz 4
For General Chemistry I (CH101)

Date: May 27 (Mon), Time: 19:00 ~ 19:45

Professor Name	Class	Student I.D. Number	Name

The periodic table is given in the last page of this quiz.

1. (Total 6 pts, 2 pts for each correct answer) **Answer the following questions.**

(a) Which molecule is most acidic?



Answer: CH_3OH

(b) Which molecule is most acidic?



Answer: CH_3COOH

(c) Which molecule is most basic?



Answer: $\text{CH}_3\text{CH}_2\text{O}^-$

2. (4 pts) **Classify each compound as a Lewis acid, a Bronsted-Lowry acid, both or neither.**



H_3O^+ : Both

Cl_3C^+ : Lewis acid

BCl_3 : Lewis acid

BF_4^- : neither

+1 pt each

No explanation required

3. (12 pts) A sample of 50.00 mL of 0.1000 M aqueous solution of chloroacetic acid, CH_2ClCOOH ($K_a = 1.4 \times 10^{-3}$), is titrated with a 0.1000 M NaOH solution. Calculate the pH at the following stages in the titration and plot the titration curve: 0, 25.00, 50.00, and 55.00 mL NaOH. In the titration curve, you must clearly indicate all the pH values that you calculated in this problem.

Let $x = [\text{H}_3\text{O}^+]$

V = 0 mL:

$$\frac{x^2}{0.1000 - x} = 1.4 \times 10^{-3}$$

$$\therefore x = 1.12 \times 10^{-2} \quad \text{pH} = -\log x = 1.95 \dots + 2 \text{ pts}$$

V = 25.00 mL:

$$\frac{\left(\frac{2.500 \text{ mmol}}{75.00 \text{ mL}} + x\right)x}{\left(\frac{2.50 \text{ mmol}}{75.00 \text{ mL}} - x\right)} = \frac{(0.0333 + x)x}{0.0333 - x} = 1.4 \times 10^{-3}$$

$$x = 1.3 \times 10^{-3} \quad \text{pH} = 2.89$$

Alternatively, considering that chloroacetic acid is a weak acid, you can use a simple formula:

$$\text{pH} \approx \text{pKa} = 2.85$$

Both ways are graded as correct. ...+2 pts

V = 50.00 mL:

At the equivalence point, the conjugate base of chloroacetic acid undergoes the following reaction:



Let $y = [\text{CH}_2\text{ClCOOH}] = [\text{OH}^-]$

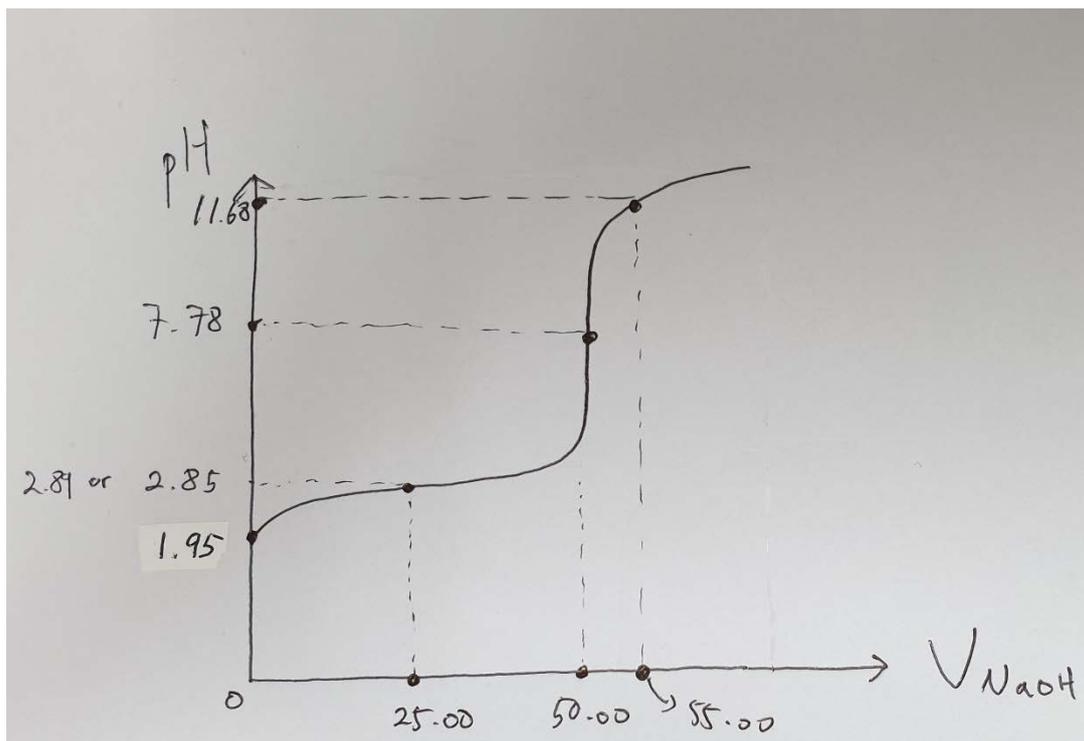
$$\frac{y^2}{0.0500 - y} = K_b = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.14 \times 10^{-12}$$

$$y = [\text{OH}^-] = 5.97 \times 10^{-7} \quad \text{pOH} = -\log y = 6.22 \quad \therefore \text{pH} = 7.78 \dots + 2 \text{ pts}$$

V = 55.00 mL:

$$[\text{OH}^-] = \frac{(5.00 \text{ mL})(0.1000 \text{ M})}{105.00 \text{ mL}} = 4.76 \times 10^{-3} \text{ M} \quad \text{pOH} = 2.32 \quad \therefore \text{pH} = 11.68 \dots + 2 \text{ pts}$$

The titration curve is as follows:



If the general shape of the curve is correct, +2 pts

If all points and numbers in the graph are correct, +2 pts

4. (Total 7 pts) The solubility product of nickel(II) hydroxide, $\text{Ni}(\text{OH})_2$, at 25°C is $K_{\text{sp}} = 1.6 \times 10^{-16}$.

(a) (3 pts) Calculate the molar solubility of $\text{Ni}(\text{OH})_2$ in pure water at 25°C .

$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-16} \dots + 1 \text{ pt}$$

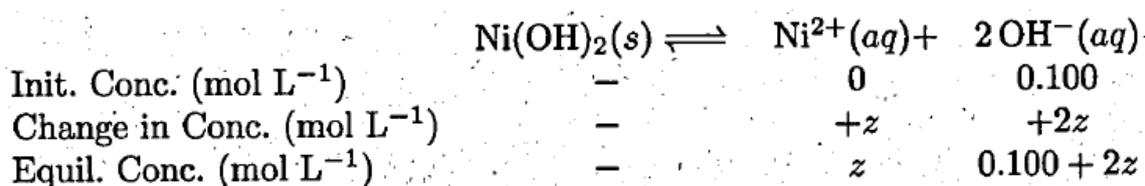
Let solubility $S = [\text{Ni}^{2+}]$

$$S \times (2S)^2 = 4S^3 = 1.6 \times 10^{-16}$$

$$\therefore S = \left(\frac{1.6 \times 10^{-16}}{4} \right)^{\frac{1}{3}} = 3.4 \times 10^{-6} \text{ M} \dots + 2 \text{ pts}$$

(b) (4 pts) Calculate the molar solubility of $\text{Ni}(\text{OH})_2$ in 0.100 M NaOH.

The presence of a common ion (the hydroxide ion) reduces the solubility. If we let z as the extent of concentration change to reach equilibrium:



Substitute the equilibrium concentrations into the K_{sp} expression:

$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{OH}^-]^2 = z(0.100 + 2z)^2 = 1.6 \times 10^{-16} \dots + 2 \text{ pts}$$

Rather than solving a cubic equation, let's assume that $2z$ is much smaller than 0.100 M. Then:

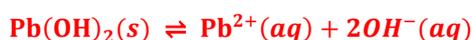
$$z(0.100)^2 = 1.6 \times 10^{-16} \quad z = \text{solubility} = 1.6 \times 10^{-14} \text{ M} \dots + 2 \text{ pts}$$

We can see that $2z$ is indeed much smaller than 0.100 M.

5. (Total 11 pts) K_{sp} for Pb(OH)_2 is 4.2×10^{-15} , and K_f for Pb(OH)_3^- is 4.0×10^{14} . Suppose a solution whose initial concentration of Pb^{2+} (aq) is 0.100 M is brought to pH 12.0 by addition of solid NaOH.

(a) (4 pts) Assuming that Pb(OH)_2 (s) is present in the solution, calculate $[\text{Pb}^{2+}]$ and $[\text{Pb(OH)}_3^-]$ at equilibrium.

Let's assume that following precipitation reaction takes place:



Since $[\text{OH}^-] = 0.010$ M at pH 12.0,

$$K_{sp} = 4.2 \times 10^{-15} = [\text{Pb}^{2+}][\text{OH}^-]^2 = [\text{Pb}^{2+}](0.010)^2$$

$$\therefore [\text{Pb}^{2+}] = 4.2 \times 10^{-11} \text{ M} \dots + 2 \text{ pts}$$

Meanwhile, formation of a coordination complex Pb(OH)_3^- is also taking place:



$$K_f = 4.0 \times 10^{14} = \frac{[\text{Pb(OH)}_3^-]}{[\text{Pb}^{2+}][\text{OH}^-]^3}$$

$$[\text{Pb(OH)}_3^-] = (4.0 \times 10^{14}) \times (4.2 \times 10^{-11}) \times (0.010)^3 = 0.017 \text{ M} \dots + 2 \text{ pts}$$

(b) (2 pts) Deducing from your answers in (a), is the assumption that solid Pb(OH)_2 is present in the solution correct or incorrect? Explain your reasoning.

From (a), we can find out that $[\text{Pb}^{2+}]$ and $[\text{Pb(OH)}_3^-]$ at equilibrium is fixed at 4.2×10^{-11} M and 0.017 M. This indicates that any excess amount of Pb^{2+} (concentration higher than 0.017 M) must precipitate out of the solution as Pb(OH)_2 . Therefore, the assumption that solid Pb(OH)_2 exists in the solution is correct.

+2 pts for correct explanation; there MUST be comparison between $[\text{Pb(OH)}_3^-]$ and initial $[\text{Pb}^{2+}]$

(c) (2 pts) If initial concentration of Pb^{2+} (aq) is 0.010 M, is the assumption that solid Pb(OH)_2 is present in the solution correct or incorrect? Explain your reasoning.

Because initial concentration of Pb^{2+} is less than 0.017 M, essentially all of the Pb^{2+} ions will form the coordination complex. Therefore, no precipitate of Pb(OH)_2 can form; the assumption

is incorrect.

+2 pts for correct explanation; there MUST be comparison between $[\text{Pb}(\text{OH})_3^-]$ and initial $[\text{Pb}^{2+}]$

(d) (3 pts) Calculate $[\text{Pb}^{2+}]$ and $[\text{Pb}(\text{OH})_3^-]$ at equilibrium when initial concentration of Pb^{2+} (aq) is 0.010 M.

Because all Pb^{2+} ions participate in the complex, $[\text{Pb}(\text{OH})_3^-] = 0.010 \text{ M}$+1 pt

Put this value into the K_f mass-action expression:

$$K_f = 4.0 \times 10^{14} = \frac{[\text{Pb}(\text{OH})_3^-]}{[\text{Pb}^{2+}][\text{OH}^-]^3} = \frac{0.010}{[\text{Pb}^{2+}](0.010)^3}$$
$$\therefore [\text{Pb}^{2+}] = \frac{1}{(4.0 \times 10^{14}) \times (0.010)^2} = 2.5 \times 10^{-11} \text{ M} \dots + 2 \text{ pts}$$

