CHM 2754

Final exam - 2018

Translated from the French

1. An electrochemical analysis of the Cu^{2+} (63.548 g mol^{-1}) content in lake water gave the following result: average = 8.07 ppm and a standard deviation, s = 0.15 ppm. The expected value, based on a large number of previous measurements and using a different technique was 8.11 ppm

a) i) What was the precision of the set of data, above?

ii) What was the accuracy of the set of data, above?

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i) Precision = the standard deviation = ± 0.15 ppm

ii) Accuracy = |expected value − measured value| = |8.11 − 8.07| = +0.04 ppm
= 0.5 %

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b) If half of the Cu^{2+} (in gm) was present in the form of sulfate ($CuSO_4$, 159.60 g mol^{-1}) and the other half in the form of chloride ($CuCl_2$, 134.5 g mol^{-1}), Calculate:

i) the mass in mg of Cu^{2+} ions present in 1.0 L of water;

ii) the mass in mg of $CuSO_4$ present in 1.0 L of water; and

iii) the concentration in ppm of $CuCl_2$ present in the water.

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i) $\text{ppm}(Cu^{2+}) = \frac{\text{mass}(Cu^{2+})}{\text{mass}(H_2O)} \times 10^6$

$\therefore \text{mass}(Cu^{2+}) = \text{ppm}(Cu^{2+}) \times \text{mass}(H_2O) \times 10^{-6}$

$= 8.07 \times 1000\ \text{g L}^{-1} \times 10^{-6}$

$= \boxed{0.00807\ \text{g L}^{-1}}$

$= 8.07\ \text{mg L}^{-1}$

(ii) $\text{ppm}(CuSO_4) = \frac{1}{2}\,\text{ppm}(\text{total } Cu^{2+}) = 8.07/2 \text{ ppm} = 4.035 \text{ mg L}^{-1}$

$\text{moles } CuSO_4 = \frac{\text{mass }(CuSO_4)}{63.546 \text{ g mol}} = \text{moles }(Cu^{2+} \text{ in sulfate}) = \frac{8.07}{2} \times \frac{159.60}{63.54}$

$= \boxed{10.1 \text{ mg L}^{-1}}$

(iii) Similarly for $CuCl_2$

$\text{ppm}(CuCl_2) = \frac{8.07}{2} \times \frac{134.45}{63.546} = 8.54 \text{ mg L}^{-1} = \boxed{8.54 \text{ ppm}}$

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2. A solid mixture (0.4789 g) containing <u>only</u> $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (392.13 g mol^{-1}) and $FeCl_2 \cdot 6H_2O$ (234.84 g mol^{-1}) was dissolved in concentrated HCl. After treatment with NH_3, the precipitate was heated to a high temperature, leaving behind 0.1234 g of Fe_2O_3 (159.69 g mol^{-1}). Calculate:

a) the mass percentage of Fe (55.847 g mol^{-1}) in the sample

b) the mass percentage of H_2O (18.01 g mol^{-1}) in the sample; and

c) the mass percentage of Cl (35.452 g mol^{-1}) in the sample.

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a) All iron in the sample becomes Fe_2O_3

$n_{Fe_2O_3} = \frac{0.1234 \text{ g}}{159.69 \text{ g mol}^{-1}} = 7.727 \times 10^{-4} \text{ mol}$

$\therefore n_{Fe} = 2\, n_{Fe_2O_3} = 2 \times 7.727 \times 10^{-4} = 1.546 \times 10^{-3} \text{ mol}$

$\therefore m_{Fe} = n_{Fe} \times 55.847 \text{ g mol}^{-1} = 55.847 \times 1.546 \times 10^{-3} = 0.08635 \text{ g}$

$\%\, Fe = \frac{0.08635 \text{ g}}{0.4789 \text{ g}} \times 100 = \boxed{18.03\,\%}$

b) $n_{H_2O} = 6\, n_{Fe}$ regardless of the compound $= 6 \times 1.546 \times 10^{-3} = 9.273 \times 10^{-3} \text{ mol}$

$\therefore m_{H_2O} = 9.273 \times 10^{-3} \text{ mol} \times 18.01 \text{ g mol}^{-1} = 0.1670 \text{ g}$

$\therefore \%\, H_2O = \frac{0.1670}{0.4789} \times 100\,\% = \boxed{34.83\,\%}$

c) % Fe in $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ $= \frac{55.847}{392.13} \times 100 = 14.2\%$

% Fe in $FeCl_2 \cdot 6H_2O$ $= \frac{55.847}{234.84} \times 100 = 23.8\%$

Let x be the mass fraction of $FeCl_2 \cdot 6H_2O$ in the sample

$\therefore (1-x)$ is the mass fraction of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$

The observed % must be the weighted average of 14.2% and 23.8%

$$x \times 23.8 + (1-x) \times 14.2 = 18.03$$

$$\therefore \boxed{x = 0.399}$$

$\therefore$ the % Cl in the sample is $0.399 \times$ the % Cl in $FeCl_2 \cdot 6H_2O$

$$= 0.399 \times \frac{2 \times 35.452}{234.84} = \boxed{12.05\%}$$

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3. For the ionization of lactic acid ($C_3H_6O_3$, 90.07 $g\,mol^{-1}$) $K_a = 1.38 \times 10^{-4}$ at 25°C. Calculate the concentrations of the protonated form, HA, and of the deprotonated form, A^-, in the following solutions in which are dissolved 1.00 g of lactic acid in 1 L of water, and then buffered to

a) pH = 1.0

b) pH = 10.0

c) pH = 3.860

$$n = \frac{1.00\,g}{90.07\,g\,mol^{-1}} = 0.01110\ mol$$

$$C_{HA} = \frac{0.01110\ mol}{1\ L} = 0.01110\ M$$

a) pH = 1.0, $\therefore [H^+] = 10^{-1}$

$$\alpha_0 = \frac{0.1}{0.1 + 1.38 \times 10^{-4}} = 0.9986 \quad \therefore [HA] = \alpha_0 C_{HA} = 0.9986 \times 0.01110 = \boxed{0.01108 M}$$

$$\alpha_1 = 1 - \alpha_0 = 0.00138 \quad \therefore [A] = \alpha_1 C_{HA} = \boxed{1.5297 \times 10^{-5} M}$$

b) $pH = 10 \quad \therefore [H^+] = 10^{-10}$

$$\alpha_0 = \frac{[H^+]}{[H^+]+K_a} = \frac{10^{-10}}{10^{-10}+1.38\times10^{-4}} = 7.246\times10^{-7}$$

$$\therefore [HA] = 7.246\times10^{-7}\times 0.01110 = \boxed{8.045\times10^{-9}\,M}$$

$\alpha_1 = 0.999999.$

$$\therefore [A^-] \approx C_{HA} = \boxed{0.01110\ M}$$

c) $pH = 3.860 \quad \therefore [H^+] = 10^{-3.860} = 1.38\times10^{-4}$

$pH = pK_a$; and this happens for a perfect buffer for which $[HA] = [A^-] = \frac{1}{2}C_{HA}$

$$\therefore [HA] = [A^-] = \tfrac{1}{2}(0.01110) = \boxed{0.00555\ M}$$

4a) Briefly describe the principles and/or chemical properties for which the equivalence point and the end-point of a titration are determined for the following types of analytical titrations.

(i) Acid-base;
(ii) Complexometric; and
(iii) Redox

In all three cases the equivalence point is the theoretical point in the titration where the number of moles of titrant = the number of moles of analyte

complexing agent acid/base reductant cation base/acid oxidant

(i) End point = the experimental point where there is a visible change in the the colour of the indicator

(ii) End point = the experimental point where there is a visible change in the colour of the indicator, or a sudden cloudiness

(iii) End-point = the experimental point where there is a sudden visible change in e.g. the EMF

4b) Give <u>two</u> characteristics or properties which are common to all of the above procedures:

Two of:

(i) A very spontaneous reaction, ie where the equilibrium constant is very large

(ii) A well defined stoichiometry

(iii) A sudden change in an observable physical property of the system at the equivalence point.

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5. Tris is a widely used buffer. Its ionization constant, $pK_a = 8.075$

$$\text{TrisH}^+ \rightleftharpoons \text{Tris} + \text{H}^+$$

a) Calculate the pH of a solution containing 5.56 g of TrisH$^+$ (157.59 g mol^{-1}) and 14.79 g of Tris (121.13 g mol^{-1}) in

(i) 1.00 L of water

(ii) 2.00 L of water

(i) $$C_{\text{TrisH}^+} = \frac{5.56\text{ g}}{157.59\text{ g mol}^{-1}} \Big/ 1\text{ L} = 0.0353\text{ M}$$

$$C_{\text{Tris}} = \frac{14.79\text{ g}}{121.13\text{ g mol}^{-1}} \Big/ 1\text{ L} = 0.1221\text{ M}$$

$$\text{pH} = pK_a + \log_{10}\frac{C_{\text{Tris}}}{C_{\text{TrisH}^+}} = 8.075 + \log_{10}\left(\frac{0.1221}{0.0353}\right) = \boxed{8.61}$$

(ii) When calculating the ratio of concentrations, the volume cancels. It doesn't matter if it's 1L or 2L.

$$\boxed{\text{pH} = 8.61}$$

b) What is the resulting pH if 10.0 mL of 1.00 M HCl is added to 1.00 L of the solution in part (a)?

$n_{HCl} = 0.01\ L \times 1.0\ M = 0.01\ mol$

This converts 0.01 mol of Tris into TrisH$^+$,

$$\therefore pH = pK_a + \log\left(\frac{C_{Tris}}{C_{TrisH^+}}\right) = 8.075 + \log_{10}\left(\frac{0.1221 - 0.01}{0.0353 + 0.01}\right) = \boxed{8.47}$$

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c) How many moles of HCl have to be added to 1.00 L of the solution in part (a) in order to lower the pH by 1.00? What is this quantity called?

Let x be the number of moles which have to be added

$$8.61 - 1.00 = 8.075 + \log\left(\frac{0.1221 - x}{0.0353 + x}\right)$$

$$7.61 - 8.075 = \log\left(\frac{0.1221 - x}{0.0353 + x}\right) = -0.465$$

$$\frac{0.1221 - x}{0.0353 + x} = 0.3428$$

$$\boxed{x = 0.0817\ mol}$$

This is called the buffer capacity.

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6. The amino acid, histidine, ionizes in 3 steps

$$H_3A^{2+} \underset{K_1}{\rightleftharpoons} H_2A^+ \underset{K_2}{\rightleftharpoons} HA \underset{K_3}{\rightleftharpoons} A^-$$

$K_1 = 1.70 \times 10^{-2}$

$K_2 = 7.94 \times 10^{-7}$

$K_3 = 6.61 \times 10^{-10}$

For the titration of 10.0 mL of a 0.100 M histidine solution, calculate the pH after the following additions of 0.100 M NaOH.

a) 10.0 mL

b) 15.0 mL

c) 20.0 mL

d) 25.0 mL, and

e) 30.0 mL

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a) First equivalence point. All of the H_3A^{2+} is converted into H_2A^+.

$$[H^+] = \sqrt{\frac{K_2\, C_{H_2A^+} + K_w}{1 + C_{H_2A^+}/K_1}} = \sqrt{\frac{7.94\times10^{-7}\times 0.10/2 + 10^{-14}}{1 + 0.05/1.7\times10^{-2}}} = 1.00\times10^{-4} \quad \boxed{pH = 4.00}$$

b) Half-way towards the 2nd equivalence point ∴ Perfect buffer

$$pH = pK_{a_2} = -\log(7.94\times10^{-7}) = \boxed{6.10}$$

c) Second equivalence point. All the H_2A^+ is converted into HA

$$[H^+] = \sqrt{\frac{K_3\, C_{HA^+} + K_w}{1 + C_{HA}/K_2}} = \sqrt{\frac{6.61\times10^{-10}\times 0.10/3 + 10^{-14}}{1 + 0.0333/7.94\times10^{-7}}} = 2.298\times10^{-8}\,M$$

$$\boxed{pH = 7.64}$$

d) Halfway towards the 3rd equivalence point ∴ Perfect buffer

$$pH = pK_{a_3} = -\log(6.61\times10^{-10}) = \boxed{9.18}$$

e) Third equivalence point. All of the HA is converted into A^- (a base)

$$[OH^-] = \sqrt{K_4\, C_{A^-}} = \sqrt{\frac{10^{-14}}{6.61\times10^{-10}}\times\frac{0.10}{4}}$$

$$= 6.15\times10^{-4}$$

$$\therefore [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{6.15\times10^{-4}} = 1.626\times10^{-11}$$

$$\therefore \boxed{pH = 10.79}$$

7. The reduction potentials for uranium and tin are:

$$UO_2^{2+} + 4H^+ + 2e^- \longrightarrow U^{4+} + 2H_2O \qquad E° = 0.334 \qquad (1)$$

$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+} \qquad E° = 0.154\ V \qquad (2)$$

a) If these substances were to be mixed under <u>Standard</u> conditions what would the overall reaction be, and what would be the corresponding cell potential?

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(1)-(2): $UO_2^{2+} + Sn^{2+} + 4H^+ \rightleftharpoons Sn^{4+} + U^{4+} + 2H_2O$

$$E° = 0.334 - 0.154\ V = \boxed{0.180\ V}$$

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b) Calculate the equilibrium constant for the overall reaction, and explain why this overall reaction is an appropriate redox titration

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very spontaneous towards the right

$$K_{eq} = \exp\left(\frac{nFE°}{RT}\right) = \exp\left(\frac{2 \times 96485 \times 0.180}{8.314 \times 298.}\right) = e^{14.02}$$

$$= \boxed{1.23 \times 10^6}$$

⇒ reaction is complete

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c) A 50.0 mL solution of 0.050 M UO_2^{2+} buffered in a 0.1 M acid, was titrated with 0.100 M Sn^{2+}. ^{2} The potential of the redox system was measured with a platinum electrode. Calculate the electrode potential when

(i) 12.50 mL of Sn^{2+} is added; and

(ii) at the equivalence point

$V_{UO_2^{2+}} = 50\,mL$; $[UO_2^{2+}] = 0.05M$; $[Sn^{2+}] = 0.1M$:

∴ $V_{Sn^{2+}} = 25\,mL$ at the equivalence point

(i) 12.50 mL is half-way towards the equivalence point

$n_{U^{4+}} = 12.5 \times 0.1 = 1.25$ mmol

$n_{UO_2^{2+}} = 50 \times 0.05 - 1.25 = 1.25$ mmol

$$E = E^{\circ}_{UO_2^{2+}/U^{4+}} - \frac{0.0257}{2} \ln\left(\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}\right)$$

$$= 0.334 - \frac{0.0257}{2} . \ln\left(\frac{1.25}{1.25 \times 0.1^4}\right)$$

$$= 0.334 - 0.118$$

$$= \boxed{0.216\ V}$$

(ii) $$E = \left(\sum_i n_i E_i^{\circ} + 0.0257 \ln [H^+]^{\sum_i p_i}\right) / \sum_i n_i$$

$$= \frac{2 \times 0.334 + 2 \times 0.154 + 0.0257 \ln (0.1)^4}{2+2}$$

$$= \frac{0.976 + 0.0257 \times (-9.21)}{4} = \frac{0.976 - 0.237}{4}$$

$$= \boxed{0.185\,V}$$

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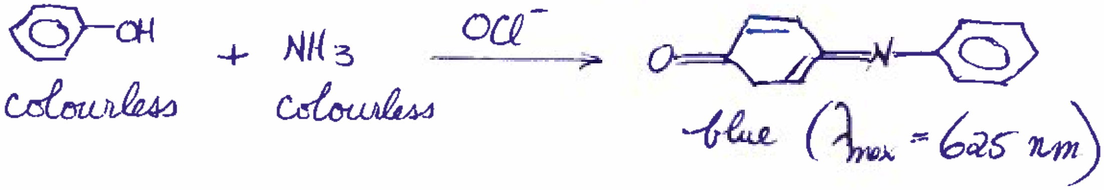
8. The following reaction of ammonia with phenol in the presence of hypochlorite (OCl^-) results in a blue product. It is used to analyze ammonia spectrophotometrically



a) A standard solution was prepared by dissolving 1.00 g of NH_4Cl (53.49 g mol^{-1}) in 100 mL of water. A 10.0 mL sample of this standard solution was titrated with a hypochlorite/phenol solution and diluted to 50.0 mL. The absorbance at 625 nm, measured in a cell of width 1.00 cm, was 0.168. Calculate the molar absorption coefficient, ε, of the blue product.

$$C = \frac{1.00\ g}{53.49\ g\ mol^{-1}} \Big/ 0.1\ L = 0.1870\ M \quad \Big| \quad C_{Blue} = C_{NH_4Cl} = C_{NH_3}$$

$$c\ (\text{diluted by a factor of } 5) = \frac{0.1870}{5} = 0.0374\ M$$

$$\varepsilon = \frac{A}{b \cdot c} = \frac{0.168}{1.0 \times 0.0374} = \boxed{4.493\ L\ mol^{-1} cm^{-1}}$$

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b) 4.37 g of a protein sample were heated in 10.0 mL of acid in order to convert the total nitrogen content into ammonia. Then the solution was diluted to 100.0 mL. As in the standard reference solution, this sample was treated with hypochlorite/phenol and diluted to 50.0 mL. The absorbance at 625 nm was 0.452. Calculate the percentage of nitrogen in the protein.

All the nitrogen was converted into NH_3

$$[NH_3] = \frac{A}{\varepsilon b} = \frac{0.452}{4.493 \times 1.0} = 0.1006\ M \text{ (in a 50 mL volume)}$$

$$\therefore n_{NH_3} = 0.1006\ M \times 50\ mL = 5.029\ mmol \text{ (had been diluted by} \times 10)$$

$$\therefore n_{NH_3} \text{ (in the original 100 mL)} = 10 \times 5.029 = 50.29\ mmol$$

$$n_N = 50.29\ mmol$$

$$m_N = 50.29 \times 10^{-3}\ mol \times 14.007\ g\ mol^{-1} = 0.7045\ g$$

$$\therefore \%N = \frac{0.7045\ g}{4.37\ g\ \text{sample}} \times 100\% = \boxed{16.12\ \%}$$

9. A compound, X, has a partition coefficient of 6.50 between water and toluene phases. A sample of X was dissolved in 100.0 mL of water and extracted one time with 10.0 mL of toluene. The concentration of X in the aqueous solution, after extraction, was 0.018 M

a) What was the concentration of X in the toluene phase?

$$\frac{[X]_{org}}{[X]_{H_2O}} = K = 6.50$$

$$\therefore [X]_{org} = 6.50 \times [X]_{H_2O} = 6.50 \times 0.018 = \boxed{0.117\ M}$$

b) Calculate the molar ratio in the two phases ie $\frac{n_{x\,(org)}}{n_{x\,(aq)}}$

$$\frac{n_x(org)}{n_x(aq.)} = \frac{0.117\,M \times 10\,mL}{0.0180\,M \times 100\,mL} = \boxed{0.65}$$

c) If the aqueous phase were extracted another 5 times with 10.0 mL of toluene, what molar fraction of X initially in the water phase would remain in the water phase?

$$[X]_0\,(aq) = 0.0180\ M$$

$$[X]_5\,(aq) = 0.0180\left(\frac{V_{aq}}{V_{aq} + KV_{toluene}}\right)^5 = 0.0180\left(\frac{100}{100 + 6.5 \times 10}\right)^5$$

$$= 0.0180 \times 0.6061^5$$

$$= 0.0180 \times 8.177 \times 10^{-2}$$

$$= \boxed{1.472 \times 10^{-3}\ M}$$

$$\text{Remaining fraction} = \frac{1.472 \times 10^{-3} \times 100\ mL}{n_x(org)_0 + n_x(aq)_0} = \frac{0.1472}{10 \times 0.117 + 0.018 \times 100}$$

$$= \frac{0.1472}{1.17 + 1.80}$$

$$= \boxed{0.0496}$$

10. Correspond the following characteristics with the different types of chromatography listed below:

A. The solutes equilibrate between a liquid mobile phase and the surface of a stationary phase

B. Charged solutes in a liquid mobile phase interact with counter-ions bound covalently to a stationary phase.

C. The mobile and stationary phases are composed of the same liquids, but access to the stationary phase depends on molecular size

D. Groups covalently bound to a stationary phase interact uniquely with specific molecules in the mobile phase.

E. The solute equilibrates between a liquid mobile phase and another liquid phase which is immobilized on the surface of a solid

Place the letter of the corresponding description in the column beside the type of chromatography.

Partition chromatography	A
Adsorption chromatography	E
Molecular exclusion chromatography	C
Affinity Chromatography	D
Ion exchange chromatography	B

$$K_w = K_a K_b = 10^{-14}$$

R = 8.314 J mol^{-1} K^{-1}
F = 96485 Coul mol^{-1}

$$K_a = \frac{[A^-][H^+]}{[HA]} = \frac{\alpha^2[HA]_0}{(1-\alpha)} = \frac{[H^+](C_A + [H^+])}{(C_{HA} - [H^+])}$$

$$\alpha_0 = \frac{[HA]}{[HA]_0} = \frac{[H^+]}{[H^+]+K}$$

$$\alpha_1 = \frac{[H^+]}{[HA]_0} = \frac{K}{[H^+]+K}$$

$$pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$$

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a[HA]_0}}{2} \approx \sqrt{K_a[HA]_0}$$

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b[B]_0}}{2} \approx \sqrt{K_b[B]_0}$$

$$[H^+] = \sqrt{\frac{K_{a2}\,C_{sel} + K_w}{1 + C_{sel}/K_{a1}}}$$

$$E = E^0 - \frac{0.0257}{n}\ln\left(\frac{[C][D]}{[A][B]}\right)$$

$$RT\ln K_{eq} = nFE^0$$

$$E_{equiv} = \frac{\sum_i n_i E_i^0 + 0.0257\,\ln[H^+]^{\Sigma p_i}}{\sum_i n_i}$$

$$A = \ell og_{10}\frac{P_0}{P} = \varepsilon bc$$

$$K = \frac{[A]_{org}}{[A]_{aq}}$$

$$[A]_i = [A]_0\left(\frac{V_{aq}}{KV_{org} + V_{aq}}\right)^i$$