Ministry of Higher Education
The Higher Institute of Engineering and technology
in New Damietta

**Department:** Chemical Engineering
**Level:** 3rd level
**Semester:** Summer Semester
**Course title:** Analytical Chemistry
**Course Code:** CHE 305

**Date:** 28/7/2018 **Day:** Saturday
**Time allowed:** 1.30 hr.
**Full marks:** 20 marks
**No. of pages:** 1

**Answer on all questions**

## Question1 (10 marks)

**1-Define:** **(4marks)**

**Solvent-**

The solvent does the dissolving; and the solvent is commonly the major fraction of the mixture.

**Titrant-** the reagent added to a solution containing the analyte and whose volume is the signal

**Equivalence point-**

The point in a titration where stoichiometricall equivalent amounts of analyte and titrant react.

**Indicator**

A colored compound whose change in color signals the end point of titration

2- Sketch a titration curve for the titration of 50.0 mL of 0.100 M $Fe^{2+}$ with 0.100 M $Ce^{4+}$ in a matrix of 1 M $HClO_4$. $E_{Fe}$=0.76V $E_{Ce}$=1.7V **(6marks)**

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq)$$

$$\text{Moles } Fe^{2+} = \text{moles } Ce^{4+}$$

or

$$M_{Fe}V_{Fe} = M_{Ce}V_{Ce}$$

Solving for the volume of $Ce^{4+}$

$$V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100\ M)(50.0\ mL)}{(0.100\ M)} = 50.0\ mL$$

$$E = E^{\circ}_{\mathrm{Fe^{3+}/Fe^{2+}}} - 0.05916 \ln \frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]}.$$

The concentrations of $Fe^{2+}$ and $Fe^{3+}$ after adding 5.0 mL of titrant are

$$[\mathrm{Fe^{2+}}] = \frac{\text{moles unreacted } \mathrm{Fe^{2+}}}{\text{total volume}} = \frac{M_{\mathrm{Fe}}V_{\mathrm{Fe}} - M_{\mathrm{Ce}}V_{\mathrm{Ce}}}{V_{\mathrm{Fe}} + V_{\mathrm{Ce}}}$$

$$= \frac{(0.100\ \mathrm{M})(50.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(5.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 5.0\ \mathrm{mL}} = 8.18 \times 10^{-2}\ \mathrm{M}$$

$$[\mathrm{Fe^{3+}}] = \frac{\text{moles } \mathrm{Ce^{4+}} \text{ added}}{\text{total volume}} = \frac{M_{\mathrm{Ce}}V_{\mathrm{Ce}}}{V_{\mathrm{Fe}} + V_{\mathrm{Ce}}}$$

$$= \frac{(0.100\ \mathrm{M})(5.0\ \mathrm{mL})}{50.0\ \mathrm{ml} + 5.0\ \mathrm{mL}} = 9.09 \times 10^{-3}\ \mathrm{M}$$

Substituting these concentrations into equation along with the formal potential for the $Fe^{3+}/Fe^{2+}$ half-reaction, we find that the potential is

$$E = +0.767\ \mathrm{V} - 0.05916 \log\left(\frac{8.18 \times 10^{-2}}{9.09 \times 10^{-3}}\right) = +0.711\ \mathrm{V}$$

At the equivalence point:

$$E_{\mathrm{eq}} = E^{\circ}_{\mathrm{Fe^{3+}/Fe^{2+}}} - 0.05916 \log \frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]}.$$

$$E_{\mathrm{eq}} = E^{\circ}_{\mathrm{Ce^{4+}/Ce^{3+}}} - 0.05916 \log \frac{[\mathrm{Ce^{3+}}]}{[\mathrm{Ce^{4+}}]}.$$

Adding together these two Nernst equations leaves us with

$$2E_{\text{eq}} = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} - 0.05916 \log \frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]}.$$

At the equivalence point, the titration reaction's stoichiometry requires that

$$[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$$

$$[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$$

The ratio in the log term of equation, therefore, equals one and the log term is zero.

$$E = E^{\circ}_{\text{Ce}^{4+}/\text{Ce}^{3+}} - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

For example, after adding 60.0 mL of titrant, the concentrations of $\text{Ce}^{3+}$ and $\text{Ce}^{4+}$ are

$$[\text{Ce}^{3+}] = \frac{\text{intial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{\text{Fe}}V_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}} = 4.55 \times 10^{-2}\text{ M}$$

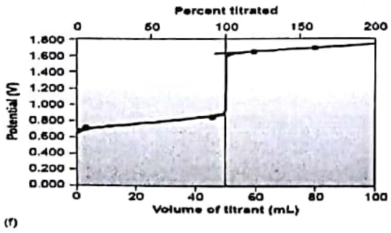
$$[\text{Ce}^{4+}] = \frac{\text{moles excess Ce}^{4+}}{\text{total volume}} = \frac{M_{\text{Ce}}V_{\text{Ce}} - M_{\text{Fe}}V_{\text{Fe}}}{V_{\text{Fe}} + V_{\text{Ce}}}$$

$$= \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}} = 9.09 \times 10^{-3}\text{ M}$$

Substituting these concentrations into equation gives the potential as

$$E = +1.70\text{ V} - 0.05916 \log \frac{4.55 \times 10^{-2}}{9.09 \times 10^{-3}} = 1.66\text{ V}$$

| Volume $\text{Ce}^{4+}$ (mL) | $E$ (V) | Volume $\text{Ce}^{4+}$ (mL) | $E$ (V) |
|---|---|---|---|
| 5.00 | 0.711 | 55.00 | 1.64 |
| 10.00 | 0.731 | 60.00 | 1.66 |
| 15.00 | 0.745 | 65.00 | 1.67 |
| 20.00 | 0.757 | 70.00 | 1.68 |
| 25.00 | 0.767 | 75.00 | 1.68 |
| 30.00 | 0.777 | 80.00 | 1.69 |
| 35.00 | 0.789 | 85.00 | 1.69 |
| 40.00 | 0.803 | 90.00 | 1.69 |
| 45.00 | 0.823 | 95.00 | 1.70 |
| 50.00 | 1.23 | 100.00 | 1.70 |



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**Question2 (10marks):**

1- Calculate and sketch qualitatively correct titration curve for the following acid-base titration: 25 mL of 0.1 M NaOH with 0.05 M HCl **(5marks)**

Moles HCl = moles NaOH

or

$$M_a V_a = M_b V_b$$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point, therefore, is

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{(0.200 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. Initially the solution is 0.100 M in HCl, which, since HCl is a strong acid, means that the pH is

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

The equilibrium constant for reaction 9.1 is $(K_w)^{-1}$, or $1.00 \times 10^{14}$. Since this is such a large value we can treat reaction 9.1 as though it goes to completion. After adding 10.0 mL of NaOH, therefore, the concentration of excess HCl is

$$[\text{HCl}] = \frac{\text{moles excess HCl}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

$$= \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.200 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.050 \text{ M}$$

giving a pH of 1.30.

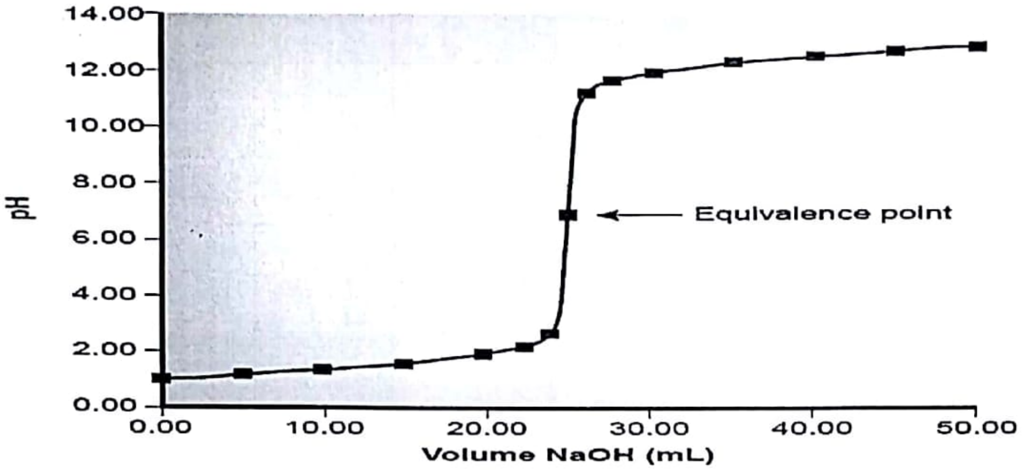
$$[\mathrm{OH^-}] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b}$$

$$= \frac{(0.200\ \mathrm{M})(30.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 30.0\ \mathrm{mL}} = 0.0125\ \mathrm{M}$$

To find the concentration of $H_3O^+$, we use the $K_w$ expression

$$[\mathrm{H_3O^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13}$$

| Volume (mL) of Titrant | pH |
|---|---|
| 0.00 | 1.00 |
| 5.00 | 1.14 |
| 10.00 | 1.30 |
| 15.00 | 1.51 |
| 20.00 | 1.85 |
| 22.00 | 2.08 |
| 24.00 | 2.57 |
| 25.00 | 7.00 |
| 26.00 | 11.42 |
| 28.00 | 11.89 |
| 30.00 | 12.50 |
| 35.00 | 12.37 |
| 40.00 | 12.52 |
| 45.00 | 12.62 |
| 50.00 | 12.70 |



**2-** Commercially available concentrated hydrochloric acid is 35% w/w HCL. Its density is 1.16 g/mL. Using this information calculate the molarity of concentrated HCl **(3marks)**

d = 1000x1.18= 1180g/L

M=0.37x1180/36.5= 11.96M

**3-** The maximum allowed concentration of chloride in a municipal drinking water supply is $2.5\times10^2$ ppm $Cl^-$. When the supply of water exceeds this limit, it often has a distinctive salty taste. **What is this concentration in moles** $Cl^-$/litre?

(atomic weight =35.5) **(2marks)**

$$\frac{2.50\times10^{2}\ \text{mg Cl}^-}{\text{L}}\times\frac{1\ \text{g}}{1000\ \text{mg}}\times\frac{1\ \text{mole Cl}^-}{35.453\ \text{g Cl}^-}=7.05\times10^{-3}\ \text{M}$$

*With my best wishes*

*Dr:Hend EL Sayed Gadow*