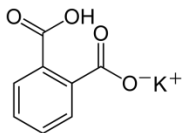


7 – Potentiometry and Redox Titrations

1] A pH electrode responded with a potential of -433 mV in a solution of 0.0500 M KHP at pH 4.01



potassium hydrogen phthalate.

The electrode is rinsed and placed in an unknown solution and responds with a potential of -692 mV. What is the pH of this unknown?¹

2] The response of a F⁻ selective electrode was found to be 0.355 V in standardize 1.00e-3 M solution. The response of this electrode in an unknown solution of F⁻ is 0.407 V. What is [F⁻] for that unknown solution?²

3] The linear pH range for the average pH electrode is about:³

- a) 0 to 14
- b) -5 to 18
- c) 2 to 10
- d) 1 to 14
- e) -10 to 10

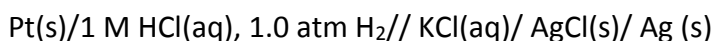
4] A very common interference for the glass pH electrode is _____.⁴

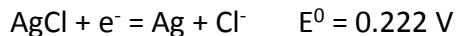
5] A glass pH electrode was found to have a potential of -0.0412 V when used with a buffer of pH 6.00. An unknown solution was found to have a potential of -0.2004 V. What is the pH of this unknown solution?⁵

6] A pH electrode responded with a voltage of 0.227 V in a standardized pH 7.000 solution. What is the pH of an unknown if that pH electrode responds with a voltage of 0.363 V?⁶

7] A Mg²⁺ ISE was found to have a potential of 0.3674 V when in contact with a solution of 6.87e-3 M. That same electrode was to have a potential of 0.4464 V in contact with an unknown solution of Mg²⁺. What is the concentration of Mg²⁺ in that unknown?⁷

8] What is [Cl⁻] if the measured potential of the following cell is 0.321 V?⁸



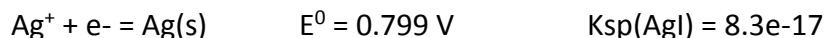


9] The potential of an F^- ISE and calomel electrode was -0.1823 V for a 25.0 mL of sample. Addition of 5.00 mL of standard solution containing $5.63 \times 10^{-5} \text{ M F}^-$ caused the combination electrode to change to -0.2446 V . What is the concentration of F^- in that sample? ⁹

10] A pH electrode was found to have a potential of 0.241 V in a pH 4.01 buffer solution. A sample solution was found to have a potential of 0.252 V . What is the pH of that sample? ¹⁰

11] A 20.00 mL solution of 0.1004 M KI was titrated with 0.0845 M AgNO_3 .

- Calculate the cell voltage when $V_{\text{Ag}^+} = 15.00 \text{ mL}$. Assume an SHE cathode and a Ag/AgI indicator electrode.
- E_{cell} when $V_{\text{Ag}^+} = 23.76$
- E_{cell} when $V_{\text{Ag}^+} = 25.00 \text{ mL}$ ¹¹



12] KMnO_4 can be standardized with which of the following? ¹²

- H_2O_2
- CH_4
- H_2O
- NaC_2O_4
- C_2H_4

13] Which is true of the equivalence point for the redox titration of Fe^{2+} with Ce^{4+} ? ¹³

- only $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$
- $[\text{Fe}^{2+}] = [\text{Ce}^{3+}]$ and $[\text{Ce}^{4+}] = [\text{Fe}^{3+}]$
- $[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$ and $[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$
- $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$ and $[\text{Ce}^{4+}] = [\text{Ce}^{3+}]$
- $[\text{Fe}^{2+}] = 0$

14] What are the final concentrations of each ion when 25.0-mL of 0.0500 M Ce^{4+} is mixed with 15.0-mL of 0.0500 M Cu^+ ?



What is the potential of the final solution when 25.0-mL of 0.0500 M Ce^{4+} is mixed with 15.0-mL of 0.0500 M Cu^+ ? ¹⁴

15] Calculate the cell potential when 25.0 mL of 0.010 M Ce^{4+} is added to 15.0 mL of 0.010 M Fe^{2+} . ¹⁵



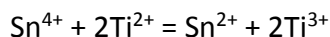
16] Derive the titration curve for the titration of 50.00 mL of 0.0500 M Fe^{2+} with 0.100 M Ce^{4+} using these volumes of titrant: ¹⁶

A] 5.00 mL of 0.100 M Ce^{4+}

B] 25.00 mL

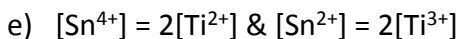
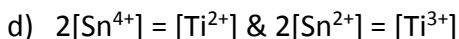
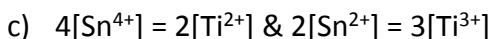
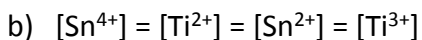
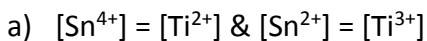
C] 25.10 mL

17] 18.00 mL of 0.125 M Sn^{4+} is titrated with 0.100 M Ti^{2+} in the following reaction:



What is the added volume of titrant required to reach the equivalence point?

Which of the following is true at the equivalence point? ¹⁷



18] Fe^{2+} was titrated with Ce^{4+} , what is potential of a Pt wire electrode immersed in this solution at the equivalence point? Assume the reference potential electrode to be 0.000 V. ¹⁸



Answers

$$^1 E = \text{const} - 0.0592 \text{ pH} \quad \text{must find const.}$$

$$-0.433 \text{ V} = \text{const} - 0.0592 (4.01) \quad \text{const} = -0.196 \text{ V}$$

Now find unkn pH

$$-0.692 = -0.196 - 0.0592 \text{ pH} \quad \text{pH} = 8.39$$

$$^2 E = \text{const} - 0.0592 \log [\text{F}^-]$$

$$0.355 = \text{const} - 0.0592 \log [1.00\text{e-}3]$$

$$\text{const} = 0.177$$

$$0.407 = 0.177 - 0.0592 \log [\text{F}^-] \quad [\text{F}^-] = 1.30\text{e-}4 \text{ M}$$

³ 2 to 10

⁴ Na⁺

$$^5 E = \text{const} - 0.0592 * \text{pH} \quad -0.0412 = \text{const} - 0.0592 * 6.00 \quad \text{const} = 0.314$$

$$-0.2004 = 0.314 - 0.0592 * \text{pH} \quad \text{pH} = 8.69$$

$$^6 E = \text{const.} - 0.0592 \text{ pH} \quad 0.227 = \text{const.} - 0.0592 * 7.000 \quad \text{const.} = 0.6414$$
$$0.363 = 0.6414 - 0.0592 \text{ pH} \quad \text{pH} = 4.702$$

$$^7 E = \text{const} - 0.0592 / 2 * \text{pMg} \quad 0.3674 = \text{const} - 0.0592 / 2 * (-\log(6.87\text{e-}3))$$

$$\text{const} = 0.431$$

$$0.4464 = 0.431 - 0.0592 / 2 * \text{pMg} \quad [\text{Mg}^{2+}] = 3.31 \text{ M}$$

$$^8 E_{\text{cell}} = E_{\text{cath.}} - E_{\text{anod.}} = 0.197 - 0.000 \text{ V} \quad E_{\text{cath.}} = 0.321 = 0.222 - 0.0592 \log [\text{Cl}^-] \quad [\text{Cl}^-] = 0.0212 \text{ M}$$

⁹ start with $E = \text{int} - 0.0592 \log[F^-]$ let $x = \text{unk } [F^-]$

2 eqns: $-0.1823 = \text{int} - 0.0592 \log(x)$

$-(-0.2446 = \text{int} - 0.0592 \log(x(25.00/30.00) + 5.63e-5(5.00/30.00))$

$6.23e-2 = 0.0592 \log(0.833x + 9.38e-6) - 0.0592 \log(x)$

$1.052 = \log[(0.833x + 9.38e-6)/(x)] \quad x = 8.97e-7 \text{ M}$

¹⁰ 3.82



Initial $\text{I}^- = 20.00 \text{ mL} * 0.1004 \text{ M} = 2.008 \text{ mmol}$

Added $\text{Ag}^+ = 15.00 \text{ mL} * 0.0845 \text{ M} = 1.27 \text{ mmol}$

Ag^+	+	I^-	=	$\text{AgI}(s)$
1.27		2.008	--	
-1.27		-1.27	--	
0		0.740	--	

$[\text{I}^-] = 0.740 \text{ mmol} / 35.00 \text{ mL} = 0.0211 \text{ M}$

$E = E^0 - 0.0592 \log 1/[\text{Ag}^+]$

$K_{sp} = 8.3e-17 = [\text{Ag}^+][\text{I}^-]$

$[\text{Ag}^+] = 8.3e-17 / 0.0211 = 3.9e-15 \text{ M}$

$E = 0.799 - 0.0592 \log \{1 / 3.9e-15\} = -0.0538 \text{ V}$



This is the eq. pt.

Ag^+	+	I^-	=	$\text{AgI}(s)$
0		0	--	
+x		+x		

$$x^2 = K_{sp} = 8.3e-17$$

$$x = 9.1e-9$$

$$E = E^0 - 0.0592 \log 1/[Ag^+]$$

$$E = 0.799 - 0.0592 \log \{1 / 9.1e-9\} = 0.323 \text{ V}$$

c) we are beyond the eq. pt.

$$\text{excess } Ag^+ = (25.00 - 23.76) \text{ mL} * 0.0845 \text{ M} = 0.105 \text{ mmol}$$

$$[Ag^+] = 0.105 \text{ mmol} / 45.00 \text{ mL} = 2.33e-3 \text{ M}$$

$$E = 0.799 - 0.0592 \log \{1 / 2.33e-3\} = 0.643 \text{ V}$$

¹² NaC_2O_4

¹³ $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$

¹⁴ Reaction: $Ce^{4+} + Cu^+ = Ce^{3+} + Cu^{2+}$

$$\text{Initial mol } Ce^{4+} = 25.0\text{-mL} * 0.0500 \text{ M} = 1.25 \text{ mmol}$$

$$\text{Initial mol } Cu^+ = 15.0\text{-mL} * 0.0500 \text{ M} = 0.75 \text{ mmol}$$

More Ce^{4+} than Cu^+ therefore

$$\text{Mol } Ce^{3+} = 0.75 \text{ mmol}$$

$$[Ce^{3+}] = 0.75 \text{ mmol} / 40.0\text{-mL} = 1.9e-2 \text{ M}$$

$$\text{Mol } Ce^{4+} = 0.50 \text{ mmol}$$

$$[Ce^{4+}] = 0.50 \text{ mmol} / 40.0\text{-mL} = 1.3e-2 \text{ M}$$

$$\text{Mol } Cu^+ = 0.00 \text{ mmol}$$

$$[Cu^+] = 0.00$$

$$\text{Mol Cu}^{2+} = 0.75 \text{ mmol}$$

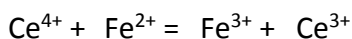
$$[\text{Cu}^{2+}] = 0.75 \text{ mmol} / 40.0\text{-mL} = 1.9\text{e-}2 \text{ M}$$

$$E = 1.44 - 0.0592 \log 1.9\text{e-}2 / 1.3\text{e-}2 = 1.43 \text{ V}$$

$$^{15} \text{ Mol Ce}^{4+} = 25.0 \text{ mL} * 0.010 \text{ M} = 0.25 \text{ mmol}$$

$$\text{Mol Fe}^{2+} = 15.0 \text{ mL} * 0.010 \text{ M} = 0.15 \text{ mmol}$$

Excess Ce^{4+} region



$$0.25 \quad 0.15 \quad 0 \quad 0$$

$$\underline{-0.15 \quad -0.15 \quad +0.15 \quad +0.15}$$

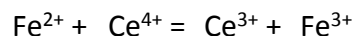
$$0.10 \quad 0 \quad 0.15 \quad 0.15$$

$$E = 1.70 - (0.0592) \log (0.15/0.10) = 1.69 \text{ V}$$

$$^{16} \text{ A] } 5.00 \text{ mL of } 0.100 \text{ M Ce}^{4+}$$

$$\text{initial mol of Fe}^{2+} = 50.00 \text{ mL} * 0.0500 \text{ M Fe}^{2+} = 2.50 \text{ mmol}$$

$$\text{added mol of Ce}^{4+} = 5.00 \text{ mL} * 0.100 \text{ M Ce}^{4+} = 0.500 \text{ mmol}$$



$$2.50 \quad 0.500 \quad 0 \quad 0$$

$$\underline{-0.500 \quad -0.500 \quad +0.500 \quad +0.500}$$

$$2.00 \quad 0 \quad 0.500 \quad 0.500$$

Both Fe^{2+} and Fe^{3+} are present this is a metal buffer.

$$E = 0.771 - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0.771 - 0.0592 \log \frac{\frac{2.00\text{mmol}}{55.00\text{mL}}}{\frac{0.500}{55.00\text{mL}}}$$

$$E = 0.734 \text{ V}$$

B) initial mol of $\text{Fe}^{2+} = 50.00 \text{ mL} * 0.0500 \text{ M Fe}^{2+} = 2.50 \text{ mmol}$

added mol of $\text{Ce}^{4+} = 25.00 \text{ mL} * 0.100 \text{ M Ce}^{4+} = 2.50 \text{ mmol}$

This is the equivalence point.

$$E = E_{\text{Ce}^{4+}/3+}^0 - 0.0592 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$+ E = E_{\text{Fe}^{3+}/2+}^0 - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$2E = E_{\text{Ce}^{4+}/3+}^0 + E_{\text{Fe}^{3+}/2+}^0 - 0.0592 \log \frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]}$$

Note that at the eq. pt.

$$[\text{Fe}^{2+}] = [\text{Ce}^{4+}] \text{ \& \ } [\text{Fe}^{3+}] = [\text{Ce}^{3+}]$$

$$\text{Therefore } 2E = E_{\text{Ce}^{4+}/3+}^0 + E_{\text{Fe}^{3+}/2+}^0 - 0.0592 \log(1)$$

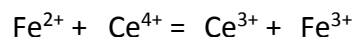
$$2E = 1.72 + 0.771$$

$$E = 1.25 \text{ V}$$

C) initial mol of $\text{Fe}^{2+} = 50.00 \text{ mL} * 0.0500 \text{ M Fe}^{2+} = 2.50 \text{ mmol}$

added mol of $\text{Ce}^{4+} = 25.10 \text{ mL} * 0.100 \text{ M Ce}^{4+} = 2.51 \text{ mmol}$

Excess Ce^{4+} region



$$2.50 \quad 2.51 \quad 0 \quad 0$$

$$\underline{-2.50 \quad -2.50 \quad +2.50 \quad +2.50}$$

$$0 \quad 0.01 \quad 2.50 \quad 2.50$$

$$E = E_{\text{Ce}^{4+}/3+}^0 - 0.0592 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$E = 1.72 - 0.0592 \log \frac{\frac{2.50 \text{ mmol}}{75.10 \text{ mL}}}{\frac{0.01 \text{ mmol}}{75.10 \text{ mL}}} = 1.58 \text{ V}$$

$$^{17} 18.00 \text{ mL} * 0.125 \text{ M Sn}^{4+} * (2 \text{ mol Ti}^{2+} / \text{mol Sn}^{4+}) * 1 / 0.100 \text{ M Ti}^{2+} = 45.0 \text{ mL}$$

$$2[\text{Sn}^{4+}] = [\text{Ti}^{2+}] \text{ \& } 2[\text{Sn}^{2+}] = [\text{Ti}^{3+}]$$



At eq. pt $[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$ and $[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$

$$E = 0.767 - 0.0592 \log [\text{Fe}^{2+}] / [\text{Fe}^{3+}]$$

$$\underline{+E = 1.70 - 0.0592 \log [\text{Ce}^{3+}] / [\text{Ce}^{4+}]}$$

$$2E = 2.467 - 0.0592 \log [\text{Fe}^{2+}] [\text{Ce}^{3+}] / [\text{Fe}^{3+}] [\text{Ce}^{4+}] = 2.467$$

$$E = 1.23 \text{ V}$$