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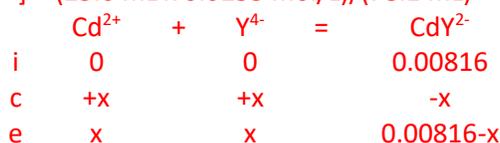
### Complete five (5) of the following seven (7) problems. 16 points each

- Consider the titration of 25.0 mL of 0.0255 M  $\text{Cd}(\text{NO}_3)_2$  with 0.0120 M EDTA in a solution buffered at pH 9.00. ( $\log K_f = 16.50$  for the  $\text{Cd}^{2+}$ -EDTA complex)
  - Calculate  $\text{pCd}^{2+}$  at two of the volumes below. (12 points)
    - At the equivalence point
    - At a volume half-way to the equivalence point
    - At a volume 11.0 mL after the equivalence point.

**First locate the equivalence point:**

$$25.0 \text{ mL} \times \frac{0.0255 \text{ mol Cd}^{2+}}{\cancel{\text{L}}} \times \frac{1 \text{ mol Y}^{4-}}{1 \text{ mol Cd}^{2+}} = \frac{1 \text{ L}}{0.0120 \text{ mol Y}^{4-}} = \mathbf{53.1 \text{ mL}}$$

**At the equivalence point:**  $[\text{CdY}^{2-}] = (25.0 \text{ mL} \times 0.0255 \text{ mol/L}) / (78.1 \text{ mL}) = 0.00816 \text{ M}$



$$K_f' = \alpha_{\text{Y}^{4-}} K_f = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}][\text{Y}^{4-}]} = (0.054)(10^{16.5}) = 1.71 \times 10^{15} = \frac{0.00816-x}{(x)(x)}$$

Solving for x yields  $[\text{Cd}^{2+}] = 2.18 \times 10^{-9} \text{ M}$  or **pCd = 8.66**

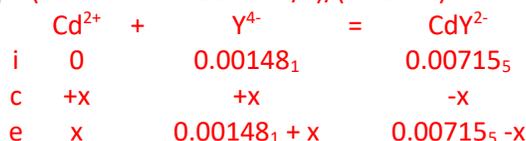
**Half-way to the equivalence point (26.6 mL):** we will have consumed half of the ( $25.0 \times 0.0255 = 0.6375$  mmol)  $\text{Cd}^{2+}$  we started with, so 0.319 mmol remains in a total of 51.6 mL of solution. Since K is large, we can assume that the dissociation of  $\text{CdY}^{2-}$  is negligible.

$$0.319 \text{ mmol Cd}^{2+} \times \frac{1}{25.0 + 26.6 \text{ mL}} = 0.00618 \text{ M Cd}^{2+} \text{ or } \mathbf{\text{pCd} = 2.21}$$

**11.2 mL after the equivalence point:** we will have 12.0 mL unreacted EDTA in a total of  $25 + 53.1 + 11 = 89.1$  mL solution.

$$[\text{CdY}^{2-}] = (25.0 \text{ mL} \times 0.0255 \text{ mol/L}) / (89.2 \text{ mL}) = 0.00715_5 \text{ M}$$

$$[\text{EDTA}] = (11.0 \text{ mL} \times 0.0120 \text{ mol/L}) / (89.1 \text{ mL}) = 0.00148_1 \text{ M}$$



$$K_f' = \alpha_{\text{Y}^{4-}} K_f = \frac{[\text{CdY}^{2-}]}{[\text{Cd}^{2+}][\text{Y}^{4-}]} = (0.054)(10^{16.5}) = \frac{0.00715_5 - x}{(x)(0.00148_1 + x)}$$

Solving for x yields  $[\text{Cd}^{2+}] = 2.82_5 \times 10^{-15} \text{ M}$  or **pCd = 14.55**

- Given that the fraction of the EDTA present as  $\text{Y}^{4-}$  does not reach its maximum until pH is over 12 or so, why would we choose to run the titration at pH 9.00 instead? (4 points)  
 Increasing the pH favors the formation of insoluble metal hydroxides, therefore, the titration must be run at a lower pH or we must use an auxiliary complexing agent to prevent hydroxide formation at higher pH.

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2. In our magnesium determination in the laboratory, we added a solution made from ammonia and ammonium chloride to each sample prior to titrating with EDTA. Explain the two primary purposes served by the addition of this solution?

Your discussion should focus on the following two ideas:

1. In order for the titration to be effective, it is important to keep as much of the EDTA in its fully deprotonated form as is reasonable. Keeping the pH high results in a larger fraction of all EDTA present as  $Y^{4-}$ . As a result, the conditional formation constant,  $K_f'$ , will remain large.
  2. At high pH, many metal ions form insoluble metal hydroxides or hydrous oxides. Should this happen, the analyte would precipitate out of solution and be unavailable for reaction with EDTA. Ammonia serves as an auxiliary complexing agent in the titration by forming a soluble magnesium complex. The tendency for ammonia to bind  $Mg^{2+}$  is greater than that for hydroxide, preventing the formation of magnesium hydroxide. However, EDTA binds more strongly than ammonia, allowing the titration reaction to occur.
3. A 1.25 g sample of soil containing  $Cu^{2+}$  and  $Zn^{2+}$  and other nonmetals was digested in acid and diluted to a final volume of 50.00 mL. This solution was treated with 25.0 mL of 0.0452 M EDTA to bind all the metal. The excess unreacted EDTA required 12.4 mL of 0.0123 M  $Mg^{2+}$  for complete reaction. An excess of the reagent 2,3-dimercapto-1-propanol was then added to displace the EDTA from zinc only. Another 29.2 mL of  $Mg^{2+}$  were required for reaction with the liberated EDTA. Calculate the percent by weight of  $Cu^{2+}$  and percent by weight of  $Zn^{2+}$  in the original rock sample. We need to figure out the mass of both metals in the sample.

$$25.0 \text{ mL} \times \frac{0.0452 \text{ mol EDTA}}{L} = 1.13 \text{ mmol EDTA delivered}$$

$$12.4 \text{ mL} \times \frac{0.0123 \text{ mol Mg}}{L} \times \frac{1 \text{ mol EDTA}}{1 \text{ mol Mg}} = 0.1525 \text{ mmol EDTA in excess}$$

So,  $(1.13 - 0.1525) \text{ mmol} = 0.9775 \text{ mmol EDTA}$  was used to bind all of the metal. Therefore,  $\text{mol } Zn^{2+} + \text{mol } Cu^{2+} = 0.9775 \text{ mmol}$

We can determine the amount of zinc from the magnesium titration:

$$29.2 \text{ mL} \times \frac{0.0123 \text{ mol } Mg^{2+}}{L} \times \frac{1 \text{ mol EDTA}}{1 \text{ mol Mg}} \times \frac{1 \text{ mol } Zn^{2+}}{1 \text{ mol EDTA}} = 0.3592 \text{ mmol } Zn^{2+}$$

So, the difference between the total moles metal and the moles zinc must correspond to the number of moles copper in the sample.

$$(0.9775 - 0.3592) \text{ mmol} = 0.6183 \text{ mmol } Cu^{2+}$$

Now to determine percent composition:

$$0.3592 \text{ mmol } Zn^{2+} \times \frac{65.37 \text{ g Zn}}{1 \text{ mol Zn}} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.02348 \text{ g Zn}$$

$$\frac{0.02348 \text{ g Zn}}{1.25 \text{ g sample}} \times 100 \% = 1.88 \% \text{ Zn}$$

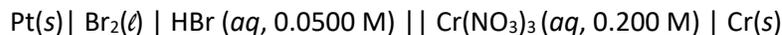
$$0.6183 \text{ mmol } Cu^{2+} \times \frac{63.54 \text{ g Cu}}{1 \text{ mol Cu}} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.03929 \text{ g Cu}$$

$$\frac{0.03929 \text{ g Cu}}{1.25 \text{ g sample}} \times 100 \% = 3.14 \% \text{ Cu}$$

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4. Consider the electrochemical cell below:



a. Calculate  $E_{\text{cell}}$  for the conditions given. (10 points)

Reaction (all species are aqueous unless noted)	$E^\circ$ (volts)
$\text{Br}_2(aq) + 2e^- = 2\text{Br}^-$	+1.098
$\text{Br}_2(\ell) + 2e^- = 2\text{Br}^-$	+1.078
$\text{NO}_3^- + 4\text{H}^+ + 3e^- = \text{NO}(g) + 2\text{H}_2\text{O}$	+0.955
$2\text{H}^+ + 2e^- = \text{H}_2(g)$	0.000
$\text{Cr}^{3+} + 3e^- = \text{Cr}(s)$	-0.740
Cathode: $\text{Cr}^{3+} + 3e^- = \text{Cr}(s)$	$E^\circ = -0.740 \text{ V}$
Anode: $\text{Br}_2(\ell) + 2e^- = 2\text{Br}^-$	$E^\circ = +1.078 \text{ V}$
Cell Rxn: $6\text{Br}^- + 2\text{Cr}^{3+} = 2\text{Cr} + 3\text{Br}_2$	$E^\circ = -0.740 \text{ V} - 1.078 \text{ V} = -1.818 \text{ V}$

Nernst equation for each half cell:

$$E_{\text{anode}} = +1.078 \text{ V} - \frac{0.05916 \text{ V}}{2} \log[\text{Br}^-]^2 = +1.078 \text{ V} - \frac{0.05916 \text{ V}}{2} \log[0.0500]^2 = +1.155 \text{ V}$$

$$E_{\text{cathode}} = -0.740 \text{ V} - \frac{0.05916 \text{ V}}{3} \log \frac{1}{[\text{Cr}^{3+}]} = -0.740 \text{ V} - \frac{0.05916 \text{ V}}{3} \log \frac{1}{[0.200]} = -0.754 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = (-0.754 - 1.155) \text{ V} = -1.909 \text{ V}$$

Or, you could use the Nernst equation for the entire cell

$$E_{\text{cell}} = -1.818 \text{ V} - \frac{0.05916 \text{ V}}{6} \log \frac{1}{[\text{Cr}^{3+}]^2 [\text{Br}^-]^6} = -1.818 \text{ V} - \frac{0.05916 \text{ V}}{6} \log \frac{1}{[0.200]^2 [0.0500]^6} = -1.909 \text{ V}$$

Either approach is acceptable.

b. Is the reaction spontaneous in the direction written in part a? How do you know? (3 points)

Since the cell potential is negative, the reaction is not spontaneous.

c. Is the reaction more favorable under standard conditions, or with the conditions given? How do you know? (3 points)

Since  $E$  is less negative and therefore  $\Delta G$  less positive, the reaction is more favorable under standard conditions.

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5. Given that  $E^\circ = +0.796 \text{ V}$  for the reaction  $\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\ell)$  and  $K_{\text{sp}} = 1.2 \times 10^{-18}$  for  $\text{Hg}_2\text{Cl}_2(\text{s})$ , calculate  $E$  for  $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Hg}(\ell) + 2\text{Cl}^-(\text{aq})$  under standard conditions.

There are several approaches to solving this problem. Here's one:

	Reaction	$E^\circ$	K	$\Delta G^\circ$
1	$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\ell)$	+0.796 V		$\Delta G^\circ_1 = -nFE^\circ$
2	$\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$		$1.2 \times 10^{-18}$	$\Delta G^\circ_2 = -RT \ln K$
Net = 1 + 2	for $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Hg}(\ell) + 2\text{Cl}^-(\text{aq})$	$E^\circ_1 + E^\circ_2$	$K_1 K_2$	$\Delta G^\circ_1 + \Delta G^\circ_2$

Since we can make our overall equation by summing the two components, we can determine the  $\Delta G^\circ$  for the reaction from the sum of the  $\Delta G^\circ$ s for the component reactions.

$$\Delta G^\circ_1 = -nFE^\circ = -(2 \text{ mol e}^-)(96485 \text{ coul/mol e}^-)(+0.796 \text{ V}) = -153,604 \text{ J}$$

$$\Delta G^\circ_2 = -RT \ln K = -(8.31441 \text{ J/mol K})(298 \text{ K}) \ln(1.2 \times 10^{-18}) = 102,240 \text{ J}$$

$$\Delta G^\circ_{\text{net}} = \Delta G^\circ_1 + \Delta G^\circ_2 = 102240 \text{ J} + (-153604 \text{ J}) = -51364 \text{ J}$$

$$E^\circ_{\text{net}} = \Delta G^\circ_{\text{net}} / (-nF) = -51364 \text{ J} / [-(2 \text{ mol e}^-)(96485 \text{ coul/mol e}^-)] = \mathbf{+0.266 \text{ V}}$$

Another approach would be to convert everything to K's and realize that  $K_{\text{net}} = K_1 \times K_2$ :

For an equilibrium:  $-nFE^\circ = -RT \ln K = -2.303RT \log K$

So, for this equilibrium at standard temperature:

$$\log K_1 = (-nFE^\circ_1) / (-2.303RT) = 26.92$$

$$K_{\text{net}} = K_1 K_2 = (10^{26.92})(1.2 \times 10^{-18}) = 9.98 \times 10^8$$

$$\text{Then } E^\circ_{\text{net}} = (2.303RT/nF) \log K = (0.05916 \text{ V}/2) \log(9.98 \times 10^8) = \mathbf{+0.266 \text{ V}}$$

Yet another approach would be to determine the  $[\text{Hg}_2^{2+}]$  from the  $K_{\text{sp}}$  under standard conditions and insert that into the Nernst equation for the redox reaction

	$\text{Hg}_2\text{Cl}_2(\text{s})$	$\rightleftharpoons$	$\text{Hg}_2^{2+}(\text{aq})$	+	$2\text{Cl}^-(\text{aq})$
I	--		0		1.00 M
C	--		+x		+ 2x
E	--		x		1.00 + 2x

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = x(1.00+2x)^2 \text{ but since } K_{\text{sp}} \text{ is so small, we may assume } 2x \ll 1 \text{ so that:}$$

$$K_{\text{sp}} = x(1.00)^2 \text{ or } x = [\text{Hg}_2^{2+}] = 1.2 \times 10^{-18} \text{ M}$$

For the redox reaction, the Nernst equation is:

$$E = +0.796 \text{ V} - \frac{0.05916 \text{ V}}{2} \log \frac{1}{[\text{Hg}_2^{2+}]} = \mathbf{+0.266 \text{ V}}$$

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6. You need to do a pH measurement and have a pH electrode, pH 4.00, 7.00, and 10.00 buffers, but **no pH meter!** You do, however, have access to a voltmeter capable of measuring potential differences at the millivolt level. Using these materials, describe how you could determine the pH of an unknown aqueous solution. Include a description of how you would collect the data and how you would use the data to find the pH of your unknown. (*hint: a pH electrode is an ISE for  $H^+$* )

In your description, you should address the following items.

1. Connect the leads of the pH electrode to the voltmeter.
  2. Measure  $E_{\text{cell}}$  for each buffer. (You should briefly describe how this is done)
  3. Plot  $E_{\text{cell}}$  vs pH, you should expect a straight line with a slope of  $\sim 59\text{mV/pH}$  unit. (Why should this relationship be linear?)
  4. Measure  $E_{\text{cell}}$  for the unknown and extract the unknown pH from your calibration curve.
7. Consider a spectrophotometry experiment like we did for the iron lab. Address the following items.
- a. How is an appropriate wavelength chosen for an absorbance measurement? Why is this choice made? (4 points) (*limit your response to three sentences or less*)  
You should talk about collecting a spectrum to determine the wavelength of maximum absorbance. At this wavelength, the measurement will be most sensitive as a small change in concentration will correspond to a larger change in absorbance. You might also mention that it is best if no other species in solution absorb at the chosen wavelength.
  - b. Why is a blank used in the measurement process? (4 points) (*limit your response to three sentences or less*)  
A blank is used to let the instrument know the response when no light is being absorbed. Since absorbance is a ratio, this measurement is critical.
  - c. How is the concentration of an unknown solution determined? What data is collected and how is it treated? (8 points)  
You should talk about making a series of standards, measuring their absorbance and plotting absorbance as a function of concentration to see the Beer's law relationship, and determine the slope and intercept. From the relationship and the absorbance of an unknown, the concentration of the unknown can be determined.

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