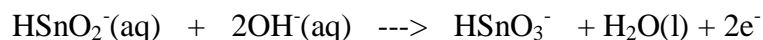


**KWANTLEN UNIVERSITY COLLEGE**  
**CHEMISTRY 1210 S-10**  
**EXAM No. 1A**  
**October 16, 1997**

**ANSWER KEY:**

**Question One:**

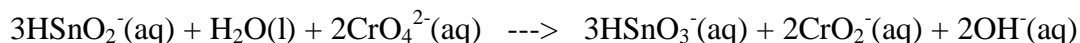
**a) Oxidation Half Reaction:**



**Reduction Half Reaction:**



**Overall Net Reaction:**



b) Since  $\text{HSnO}_2^-$  has been oxidized it acts as the **reducing agent**.

c) One mole of  $\text{CrO}_4^{2-}$  will require three moles of electrons in the reduction half-reaction, therefore:

$$\frac{194.20 \text{ g K}_2\text{CrO}_4}{1 \text{ mol K}_2\text{CrO}_4} \times \frac{1 \text{ mol K}_2\text{CrO}_4}{3 \text{ eq e}^-} = 64.73 \text{ g K}_2\text{CrO}_4 / \text{eq}$$

**Question Two:**

a) At the endpoint (equivalence point) of the titration:

$$\begin{aligned} \# \text{ equivalents K}_2\text{Cr}_2\text{O}_7 &= \# \text{ equivalents of HNO}_2 \\ (0.02147 \text{ L K}_2\text{Cr}_2\text{O}_7 \text{ soln.}) (0.2000 \text{ eq K}_2\text{Cr}_2\text{O}_7 / \text{L soln.}) &= 4.294 \times 10^{-3} \text{ eq K}_2\text{Cr}_2\text{O}_7 \\ &= 4.294 \times 10^{-3} \text{ eq HNO}_2 \end{aligned}$$

b) The  $\text{HNO}_2$  half-reaction in the titration is,



$$1 \text{ mol HNO}_2 = 2 \text{ eq e}^- = 2 \text{ eq HNO}_2$$

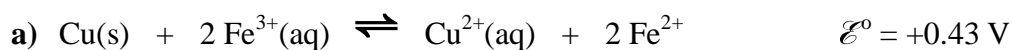
$$4.294 \times 10^{-3} \text{ eq HNO}_2 \times \frac{1 \text{ mol HNO}_2}{2 \text{ eq HNO}_2} \times \frac{1 \text{ mol NaNO}_2}{1 \text{ mol HNO}_2} = 2.147 \times 10^{-3} \text{ mol NaNO}_2$$

c) Mass of NaNO<sub>2</sub> in the sample:

$$2.147 \times 10^{-3} \text{ mol NaNO}_3 \times \frac{69.00 \text{ g NaNO}_2}{1 \text{ mol NaNO}_2} = 0.1481 \text{ g NaNO}_2$$

$$\% \text{ NaNO}_2 = (0.1481 \text{ g NaNO}_2 / 1.124 \text{ g sample}) \times 100\% = 13.18\%$$

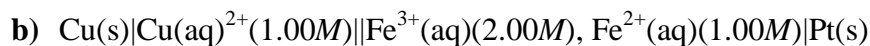
### Question Three:



$$\mathcal{E}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cell}} - \frac{0.05916}{n} \log_{10} \frac{[\text{Cu}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

$$= +0.43 \text{ V} - \frac{0.05916}{2} \log_{10} \frac{(1.00)(1.00)^2}{(2.00)^2}$$

$$= +0.45 \text{ V}$$



d) positive

e) 
$$\mathcal{E}_{\text{cell}} = 0.0 \text{ V} = \mathcal{E}^{\circ}_{\text{cell}} - \frac{0.05916}{n} \log_{10} K_c$$

or,

$$\log_{10} K_c = \frac{n\mathcal{E}^{\circ}_{\text{cell}}}{0.05916} = \frac{2(+0.43\text{V})}{0.05916} = 14.54$$

therefore,  $K_c = 3.4 \times 10^{14}$

$$\text{f) } \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cell}}^{\circ} - \frac{0.05916}{n} \log_{10} \frac{[\text{Cu}^{2+}][\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$+0.54 \text{ V} = +0.43 \text{ V} - \frac{0.05916}{2} \log_{10} \frac{[\text{Cu}^{2+}] (1.00)^2}{(2.00)^2}$$

$$\log_{10} \frac{[\text{Cu}^{2+}]}{4} = \frac{2(0.43 \text{ V} - 0.54 \text{ V})}{0.05916} = -3.72$$

therefore,  $[\text{Cu}^{2+}] = 7.64 \times 10^{-4} \text{ M}$

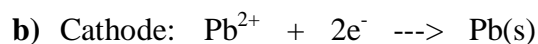
#### Question Four:



$$14475 \text{ coulombs} \times \frac{1 \text{ mol e}^{-}}{96485 \text{ coulombs}} \times \frac{1 \text{ mol M(s)}}{2 \text{ mol e}^{-}} = 7.501 \times 10^{-2} \text{ mol M(s)}$$

$$\therefore \text{ at. wt.} = \frac{15.54 \text{ g M}}{7.501 \times 10^{-2} \text{ mol M}} = 207.2 \text{ g M/mol M}$$

Pb - lead



d) Cathode (-)

$$\text{e) } C = I \times t(\text{sec})$$

$$t(\text{sec}) = C/I = \frac{14475 \text{ coulombs}}{2.00 \text{ coulombs/s}} = 7.24 \times 10^3 \text{ s}$$

$$(7.24 \times 10^3 \text{ s})(1 \text{ hr} / 3600 \text{ s}) = 2.01 \text{ hr}$$

**Question Five:**

a) i) First Order Reaction:

$$\ln[A_0] - \ln[A_t] = \ln \frac{[A_0]}{[A_t]} = kt$$

Half-Life:  $[A_t] = \frac{1}{2}[A_0]$  occurs at  $t_{1/2}$

$$\ln \frac{[A_0]}{\frac{1}{2}[A_0]} = \ln 2 = 0.693 = kt_{1/2}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{35.0\text{s}} = 0.0198 \text{ s}^{-1}$$

ii) If 95% of  $\text{PH}_3$  has decomposed, then 5% of the reactant remains, or,  
 $[A_t] = 0.0500 [A_0]$

$$\ln \frac{[A_0]}{[A_t]} = kt, \text{ or}$$

$$t = \frac{1}{k} \ln \frac{[A_0]}{[A_t]} = \frac{1}{0.0198 \text{ s}^{-1}} \ln \frac{[A_0]}{0.0500 [A_0]} = \frac{\ln(20.0)}{0.0198 \text{ s}^{-1}}$$

$$= 151 \text{ s}$$

b)  $\text{rate}_{\text{cat.}} \propto k_{\text{cat.}}$

$$\text{rate}_{\text{uncat.}} \propto k_{\text{uncat.}}$$

Since  $k = Ae^{-E_a/RT}$

$$\frac{\text{rate}_{\text{cat.}}}{\text{rate}_{\text{uncat.}}} = \frac{k_{\text{cat.}}}{k_{\text{uncat.}}} = 10^4 = \frac{Ae^{-E_{a,\text{cat}}/RT}}{Ae^{-E_{a,\text{uncat}}/RT}}$$

$$\therefore e^{-(E_{a,\text{cat}} - E_{a,\text{uncat}})/RT} = 10^4$$

$$\text{or } e^{-\Delta E_a/RT} = 10^4$$

$$-\Delta E_a/RT = \ln(10^4) = 9.21$$

$$\therefore \Delta E_a = -9.21 RT = -9.21 (8.314 \text{ J/mol-K})(300\text{K}) = -2.30 \times 10^4 \text{ J/mol} = -23.0 \text{ kJ/mol}$$

**Question Six:**

a) reaction rate =  $-d[\text{C}_2\text{O}_4^{2-}]/dt = k[\text{HgCl}_2]^x [\text{C}_2\text{O}_4^{2-}]^y$

In experiments #1 & #2,  $[\text{HgCl}_2]$  remains constant; doubling  $[\text{C}_2\text{O}_4^{2-}]$  increases the rate of reaction by a factor of four, therefore,

$$\therefore y = 2$$

Using the data from experiments #2 & #3:

$$\frac{7.1 \times 10^{-5}}{3.5 \times 10^{-5}} = \frac{k(0.105)^x (0.30)^2}{k(0.052)^x (0.30)^2}$$

$$2.03 = 2.02^x \quad \therefore x = 1$$

reaction rate =  $-d[\text{C}_2\text{O}_4^{2-}]/dt = k[\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2$

b) Using the data from experiment #1:

$$k = \frac{\text{reaction rate}}{[\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2} = \frac{(1.8 \times 10^{-5} \text{ mol/L-s})}{(0.105 \text{ mol/L})(0.15 \text{ mol/L})^2} = 7.6 \times 10^{-3} \text{ L}^2 / \text{mol}^2\text{-s}$$

b) reaction rate =  $-d[\text{C}_2\text{O}_4^{2-}]/dt = 1/2 d[\text{Cl}^-]/dt$

$$\therefore d[\text{Cl}^-]/dt = 2 \times \text{reaction rate} = (2)(3.5 \times 10^{-5} \text{ mol/L-s}) = 7.0 \times 10^{-5} \text{ mol/L-s}$$

c) reaction rate =  $-d[\text{C}_2\text{O}_4^{2-}]/dt = k[\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2$

$$= (7.6 \times 10^{-3} \text{ L}^2/\text{mol}^2\text{-s})(0.08 \text{ mol/L})(0.10 \text{ mol/L})^2$$

$$= 6.1 \times 10^{-6} \text{ mol/L-s}$$

**Question Seven:**

Rate is based on the slow, rate determining, second step, i.e., **rate =  $k_3[\text{O}_3][\text{O}]$** . O is a reactive intermediate, so we must eliminate it from the rate expression.

Steady State Approximation:  $d[\text{O}]/dt \approx 0$ , therefore,

Rate of O production = Rate of O consumption

$$K_1[\text{O}_3] = k_2[\text{O}_2][\text{O}] + k_3[\text{O}_3][\text{O}]$$

Neglect this term since  
this is from the slow step.

$$\therefore [\text{O}] = \frac{k_1[\text{O}_3]}{k_2[\text{O}_2]}$$

Substitution into the above rate expression gives:

$$\begin{aligned} \text{rate} = k_3[\text{O}_3][\text{O}] &= k_3[\text{O}_3] \frac{k_1[\text{O}_3]}{k_2[\text{O}_2]} \\ &= \frac{k_1 k_3}{k_2} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \end{aligned}$$