2008

$3\,Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3\,Cu^{2+}(aq) + 2NO(g) + 4H_2O(\ell)$

$E^\circ = +.62V$

(a) $E^\circ_{cell} = .62V = E^\circ_{RED\ cat} - E^\circ_{RED\ anode} = E^\circ_{RED} - .34V$

$E^\circ_{RED} = .62V + .34V = \boxed{.96V}$ (1 point)

(b) $\Delta G^\circ = -nFE^\circ = -(6\ mole^-)\left(96{,}500\ \frac{C}{mole^-}\right)\left(.62\ \frac{J}{C}\right)$ (V)

$\boxed{\Delta G^\circ = -360\ kJ/mol \text{ or } -360\ kJ}$ 1 point

(c) The $\Delta S^\circ > 0$ or + since 2 moles NO(g) are formed. NOTE: the $\Delta S^\circ > 0$ even though less moles are produced 13 (Reactants) → 9 (product) (1 point)

(d) Kinetics Review $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$

Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O_2 (mol L^{-1})	Initial Rate of Formation of NO_2 (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

(a) Look at Experiments 1 & 3 $\left(\frac{0.0600}{0.0200}\right)^x = \frac{7.67 \times 10^{-1}\ \frac{M}{sec}}{8.52 \times 10^{-2}\ \frac{M}{sec}}$

(i) $3^x = 9$; $\boxed{x = 2}$ (1 point) Second order w/ Respect to NO

(b) Look at Experiments 1 & 2 $\left(\frac{0.0900}{0.0300}\right)^y = \frac{2.52 \times 10^{-1}}{8.52 \times 10^{-2}}$

(ii) $3^y = 3$; $\boxed{y = 1}$ ← First order w/ Respect to O_2 (1 point)

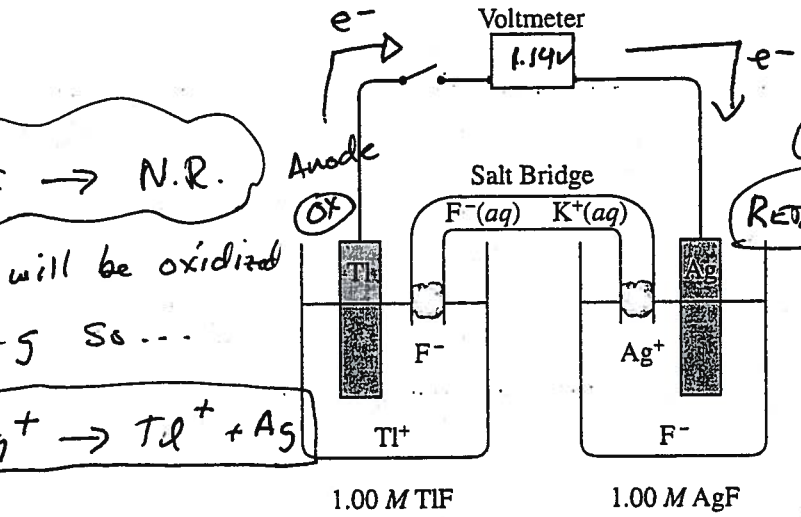
(e) $\boxed{\text{Rate} = k[NO]^2[O_2]}$ 1 point

(f) $7100\ \frac{1}{M^2 sec}$

16 points

Key!

6. Answer the following questions about electrochemical cells.



Ag + TlF → N.R.

So ∴ Tl will be oxidized ✓ not Ag So...

Tl + Ag⁺ → Tl⁺ + Ag

Ag⁺ + e⁻ → Ag .80V

Tl → Tl⁺ + e⁻ ???

1.14V

E°_{ox} for Tl is .34V

It is observed that when silver metal is placed in aqueous thallium(I) fluoride, TlF, no reaction occurs. When the switch is closed in the cell represented above, the voltage reading is +1.14 V.

(a) Write the reduction half-reaction that occurs in the cell. $e^- + Ag^+ \rightarrow Ag$

(b) Write the equation for the overall reaction that occurs in the cell.

(c) Identify the anode in the cell. Justify your answer. Tl ~~is~~ since oxidation is taking place there!

✓ (d) On the diagram above, use an arrow to clearly indicate the direction of electron flow as the cell operates.

(e) Calculate the value of the standard reduction potential for the Tl^+/Tl half-reaction.

$E^\circ_{Total} = 1.14V = .80V + E^\circ_{ox\ Tl} = .80V - E^\circ_{RED\ Tl}$ so

The standard reduction potential, E°, of the reaction $Pt^{2+} + 2e^- \rightarrow Pt$ is 1.20 V. $Tl^+ + e^- \rightarrow Tl$ $E^\circ_{Red} = -.34V$

(f) Assume that electrodes of pure Pt, Ag, and Ni are available as well as 1.00 *M* solutions of their salts. Three different electrochemical cells can be constructed using these materials. Identify the two metals that when used to make an electrochemical cell would produce the cell with the largest voltage. Explain how you arrived at your answer.

$Ni^{2+} + 2e^- \rightarrow Ni$ $E^\circ = -.25V$ $Ni/Ni^{2+} // Pt^{2+}/Pt$ Use most + RED potential (Pt) & most negative (Ni) get greatest E°_{total}.

(g) Predict whether Pt metal will react when it is placed in 1.00 *M* $AgNO_3(aq)$. Justify your answer.

$Pt + 2Ag^+ \rightarrow Pt^{2+} + 2Ag$

$Pt \rightarrow Pt^{2+} + 2e^-$ $E^\circ = -1.2$

$2Ag^+ + 2e^- \rightarrow 2Ag$ E° .80V

−.40V

No Rxn you have an E°_{total} a neg that is negative

STOP

END OF EXAM

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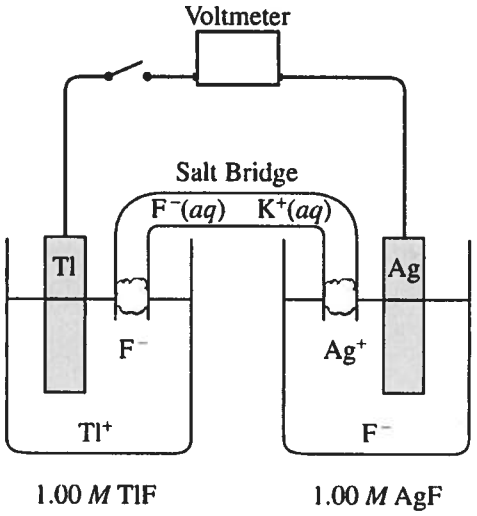
Question 6 (9 points)

Answer the following questions about electrochemical cells.



It is observed that when silver metal is placed in aqueous thallium(I) fluoride, TlF, no reaction occurs. When the switch is closed in the cell represented above, the voltage reading is +1.14 V.

(a) Write the reduction half-reaction that occurs in the cell.

$Ag^+ + e^- \rightarrow Ag$	One point is earned for the correct equation.

(b) Write the equation for the overall reaction that occurs in the cell.

$Tl + Ag^+ \rightarrow Tl^+ + Ag$	One point is earned for the correct equation.

(c) Identify the anode in the cell. Justify your answer.

The anode is where oxidation occurs. In the overall reaction Tl is oxidized to Tl^+, so the anode is the Tl electrode in the left cell.	One point is earned for the correct answer with justification.

(d) On the diagram above, use an arrow to clearly indicate the direction of electron flow as the cell operates.

The arrow should show electron flow in the direction from the Tl electrode through the wire to the Ag electrode.	One point is earned for a correct arrow.

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Question 6 (continued)

(e) Calculate the value of the standard reduction potential for the Tl^+/Tl half-reaction.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$ $+1.14\ V = +0.80V - E^\circ_{ox}$ $E^\circ_{ox} = \mathbf{-0.34\ V}$	One point is earned for the correct setup. One point is earned for the correct answer.

The standard reduction potential, E°, of the reaction $Pt^{2+} + 2\,e^- \rightarrow Pt$ is 1.20 V.

(f) Assume that electrodes of pure Pt, Ag, and Ni are available as well as 1.00 *M* solutions of their salts. Three different electrochemical cells can be constructed using these materials. Identify the two metals that when used to make an electrochemical cell would produce the cell with the largest voltage. Explain how you arrived at your answer.

E°(V) $Ni^{2+} + 2\,e^- \rightarrow Ni$ −0.25 $Ag^+ + e^- \rightarrow Ag$ 0.80 $Pt^{2+} + 2\,e^- \rightarrow Pt$ 1.20 $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$ The two metals that yield the largest E°_{cell} are those with the biggest difference in E°, namely, Pt and Ni (see E°_{cell} calculation below). $E^\circ_{cell} = +1.20 - (-0.25) = +1.45\ V$	One point is earned for the correct answer with justification.

(g) Predict whether Pt metal will react when it is placed in 1.00 *M* $AgNO_3(aq)$. Justify your answer.

When Pt metal is added to 1.00 *M* $AgNO_3$, the only redox reaction that could occur would be for Pt to become oxidized as Ag^+ is reduced. $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox} = +0.80\ V - (+1.20\ V) = -0.40\ V$ Because E°_{cell} for that reaction is negative, no reaction will occur.	One point is earned for comparing E° values. One point is earned for the correct interpretation.