CHEM 123 SU11 Fus Exam #2

(1) $\overset{(+7)}{2MnO_4^-}(aq) + \overset{(-1)}{5H_2O_2}(aq) + 6H^+(aq) \rightarrow \overset{(+2)}{2Mn^{2+}}(aq) + \overset{(0)}{5O_2}(g) + 8H_2O(l)$

In this rxn: Mn^{7+} is reduced to Mn^{2+}

oxygen is oxidized from -1 to 0

MnO_4^- acts as an oxidizing agent

H_2O_2 acts as the reducing agent **B**

(2) A rxn will occur if $\mathcal{E}^\circ_{cell}$ = (+)

Of the listed examples, only (e) meets this criteria

red: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$ $\mathcal{E}^\circ = +0.77V$

ox: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $\mathcal{E}^\circ = -0.34V$

$2Fe^{3+}(aq) + Cu(s) \rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$ $\mathcal{E}^\circ = +0.43V$

E

(3) $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(g)$

ox: $2I^-(aq) \rightarrow I_2(g) + 2e^-$ $\quad E^\circ = -0.54V$

red: $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$ $\quad E^\circ = +0.77V$

$E^\circ = +0.23V$

C

(4) $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $\quad E^\circ_{red} = -1.66V$

cathode ↙

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad E^\circ_{red} = +0.80V$

ox: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ $\quad E^\circ = +1.66V$

$3Ag^+(aq) + 3e^- \rightarrow 3Ag(s)$ $\quad E^\circ = +0.80V$

$Al(s) + 3Ag^+(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$ $\quad E^\circ = 2.46V$

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{3} \log\left(\frac{[Al^{3+}]}{[Ag^+]^3}\right)$$

$$E_{cell} = 2.46V - \frac{0.0592}{3} \log\left(\frac{0.010}{(0.010)^3}\right)$$

$$E_{cell} = 2.46V - 0.0789V$$

$$E_{cell} = 2.38V$$

A

(5) $Q = \frac{[Ag^+]}{[Al^{3+}]}$ as $Q \uparrow$, $\mathcal{E}_{cell} \downarrow$

so we want to decrease Q to $\uparrow \mathcal{E}_{cell}$

$\downarrow [Ag^+]$ or $\uparrow [Al^{3+}]$

D

(6) $3Fe(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Fe^{2+}(aq) + 2NO(g) + 4H_2O(l)$

$$3.5\,g\,Fe \times \frac{1\,mol\,Fe}{55.845\,g} \times \frac{8\,mol\,H^+}{3\,mol\,Fe} \times \frac{L}{12.0\,mol\,H^+} \times \frac{1000\,mL}{1\,L} = 13.9\,mL$$

C

(7) $$45.1\,g\,Cr \times \frac{1\,mol\,Cr}{52.0\,g} \times \frac{3\,mole^-}{1\,mol\,Cr} \times \frac{96,485\,C}{1\,mole^-} = 251,046\,C$$

$$amp = \frac{C}{sec} = \frac{251,046\,C}{853\,min\left(\frac{60\,sec}{min}\right)} = 4.91\ amps$$

C

(8) $$7.83\,C/sec \times \left(60\,min \times \frac{60\,sec}{1\,min}\right) \times \frac{1\,mol\,e^-}{96,485\,C} \times \frac{1\,mol\,Ni^{2+}}{2\,mole^-} = 0.146\,mol\,Ni^{2+}$$

$$\frac{0.146\,mol\,Ni^{2+}}{0.546\,L} = 0.268\,M$$

$[Ni^{2+}]_{remaining} =$ 0.480 M (initial) − 0.268 M (used up) $= 0.212\,M$

B

(9) ox: $Cu(s) \rightarrow Cu^{2+}_{anode} + 2e^-$

red: $Cu^{2+}_{cathode} + 2e^- \rightarrow Cu(s)$

$$Cu(s) + Cu^{2+}_{cathode} \rightarrow Cu^{2+}_{anode} + Cu(s)$$

$$Q = \frac{[Cu^{2+}]_{anode}}{[Cu^{2+}]_{cathode}}$$

to increase $\mathcal{E}_{cell}$, Q must decrease

$\downarrow [Cu^{2+}]_{anode}$ or $\uparrow [Cu^{2+}]_{cathode}$

(i) $\uparrow [Cu^{2+}]_{anode}$ X

(ii) pH does not influence Q X

(iii) adding NH_3 to cathode produces $Cu(NH_3)_4^{2+}$ and $\downarrow [Cu^{2+}]_{cathode}$ X

(iv) $\mathcal{E}^\circ_{cell} = 0$ X

E none of the above

(10) $MnO_4^-(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + MnO_2(s)$

ox: $3\,Cr^{2+}(aq) \rightarrow 3Cr^{3+}(aq) + 3e^-$ $\quad E^\circ = +0.41V$

red: $MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$ $\quad E^\circ = 0.59V$

$E^\circ = 1.00V$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

At Eq $\quad Q = K$, $E_{cell} = 0$

$$E^\circ_{cell} = \frac{RT}{nF} \ln K$$

$$\ln K = 1.00V \left(\frac{3(96,485)}{8.314(298)} \right)$$

$$K = 5.4 \times 10^{50}$$ **C**

(11) ox: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad E^\circ = +0.76V$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q \qquad Q = \frac{[Zn^{2+}]}{[M^{2+}]}$$

$$0.657V = E^\circ_{cell} - \frac{8.314(328)}{2(96,485)} \ln \left(\frac{0.5}{2.0} \right)$$

$$0.657V = E^\circ_{cell} + 0.0196V$$

$$E^\circ_{cell} = 0.637V$$

$$\mathcal{E}^\circ_{cell} = +0.76V + \mathcal{E}^\circ_{red} = 0.637V$$

$$\mathcal{E}^\circ_{red} - 0.637V - 0.76V$$

$$\mathcal{E}^\circ_{red} = -0.12V$$

$$Pb^{2+} + 2e^- \rightarrow Pb(s) \quad \mathcal{E}^\circ_{red} = -0.12V$$

D

12 $AlPO_4(s) \rightleftharpoons Al^{3+}(aq) + PO_4^{3-}(aq)$ $\mathcal{E}^\circ = \frac{0.0592}{3}\log(9.8\times10^{-21})$

$= -0.395V$

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $\mathcal{E}^\circ = -1.66V$

$AlPO_4(s) + 3e^- \rightarrow Al(s) + PO_4^{3-}(aq)$ $\mathcal{E}^\circ = -2.05V$

C

13 $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $\mathcal{E}^\circ = 0.00V$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\mathcal{E}^\circ = +0.34V$

$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)$ $\mathcal{E}^\circ = +0.34V$

$$\mathcal{E}_{cell} = \mathcal{E}^\circ_{cell} - \frac{0.0592}{n}\log Q$$

$$0.870V = 0.34V - \frac{0.0592}{2}\log\left(\frac{[H^+]^2 \blacksquare}{[Cu^{2+}]P_{H_2}}\right)$$

$$-\frac{2(0.53V)}{0.0592} = \log\left(\frac{[H^+]^2}{[0.5](1.0)}\right)$$

$$-17.9 = \log\left(\frac{[H^+]^2}{0.5}\right)$$

$$0.5(1.24\times10^{-18}) = [H^+]^2$$

$$[H^+] = 7.9\times10^{-10}$$

$$pH = 9.1$$ **D**

(14) Co: $[Ar]\ 4s^2 3d^7$

Co^{3+}: $[Ar]\ 3d^6$ **E**

(15) $[NiCl_2(CO_3)_2]^{4-}$

Cl^- monodentate, CO_3^{2-} bidentate

$CN = 6 \Rightarrow$ octahedral

Ni^{2+}: $[Ar]\ 3d^8$

D

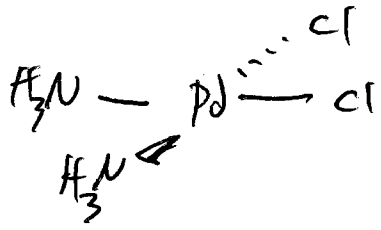
(16) $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$

This complex has 4 N, each with a lone pair ∴ H will have a CN = 4

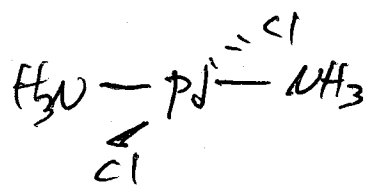
C

(17) $Pd(NH_3)_2Cl_2$

Pd^{2+}: $4d^8 \Rightarrow$ sq. planar → no optical isomers



cis



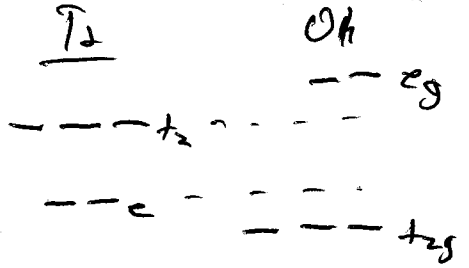
trans

B

(18) i) $-x^2y^2$
$-xy$
$-z^2$ ✓ True

$\overline{xz}\ \overline{yz}$

ii)



Δ_o is larger than Δ_t ∴ low spin is more likely in O_h False

iii) O_h
✓ $x^2-y^2\ z^2$ True

$\overline{xy}\ \overline{xz}\ \overline{yz}$

D

(19) 3 ions / formula unit $[\ \uparrow\ ]X_2$

↑ 1 complex ion; ↑ 2 counter ions

2 mol AgBr(s) per formula unit

2 Br^- counter ions

$[\quad]BC_2$

B

(20) $[Co(NH_3)_4]^{2+}$: T_d 3d TM center

$[Co(H_2O)_6]^{2+}$: O_h 3d TM center

$[IrF_6]^{4-}$: O_h 5d TM center

$[Cr(CO)_6]^{3+}$: O_h 3d TM center w/ s.f. ligand

(c), (d), and (e) can be immediately eliminated due to 5d TM + s.f. Ligands

This leaves (a) and (b)

Δ_t is much smaller than Δ_o

Ir and CO will both cause a large Δ_o, but (b) can be eliminated because the splitting for $Co(H_2O)_6^{2+} > Co(NH_3)_4^{2+}$

A

(21) $[Co(H_2O)_6]^{2+}$: Co^{2+}: $3d^7$ high spin O_h

↑↓ e_g (3) ✓

↑↓ ↑↓ ↑ t_{2g}

$[IrF_6]^{4-}$ Ir^{2+}: $4d^7$ low spin O_h

↑↓ e_g (1)

↑↓ ↑↓ ↑ t_{2g}

$[PtCl_4]^{2-}$ Pt^{2+}: $5d^8$ sq. planar

x^2-y^2 —

$+y$ ↑↓ (0)

z^2 ↑↓

$+x$ ↑↓ ↑↓ xz

$[Ni(H_2O)_6]^{2+}$ Ni^{2+}: $3d^8$ w.f. L ⇒ high spin O_h

↑↓ ↑

e_g (2)

↑↓ ↑↓ ↑ t_{2g}

A

(22) i) W^{3+}: $5d^3$ always ← low spin ⇒ no change

ii) Mn^{2+}: $3d^5$ — — ↑↑

↑↓ ↑↓ ↑ ↑ ↑ ↑

low spin high spin

E

iii) Cu^{2+}: $3d^9$ low/high spin give same # of unpaired e⁻

iv) Zn^{2+}: $3d^{10}$ low/high spin give same # of unpaired e⁻

(23) diamagnetic : zero unpaired e^-

$\mathcal{E}\Delta_1 > \mathcal{E}\Delta_2$

(a) Fe^{2+} w.f. L ⇒ high spin ⇒ unpaired e^- ✗
↳ paramagnetic

(b) ① $Fe(CN)_6^{4-}$ ② $Ru(CN)_6^{4-}$
↑ 3d ↑ sf L ↑ 4d ↑ s.f. L

both low spin, but $\mathcal{E}\Delta_2 > \mathcal{E}\Delta_1$ ✗

(c) Fe^{2+} w.f. L ⇒ high spin ⇒ unpaired e^- → paramagnetic ✓

(d) ① $Ru(CN)_6^{4-}$ ② $RuBr_6^{4-}$ $Ru^{2+}: d^6$
↑ 5d TM ↑ s.f. L ↑ 5d TM : both low spin

— e_g
↑↓ ↑↓ ↑↓ t_{2g} ✓

D

(A) $FeBr_6^{4-}$ is high spin d^6 → paramagnetic ✓

(24) $Co(CN)_4^-$ T_d | $Co(CN)_4^-$ sq. pl. | $Co(CN)_6^{3-}$ O_h

$Co^{3+}: 3d^6$

↑↑↑ t_2
↑↓ e

$3d^6$ ✗
s.f. L ✓
not sq. planar

— e_g

↑↓ ↑↓ ↑↓ t_{2g}

$\mathcal{E}$ ↑

Filling the 6 e⁻ in the O_h diagram gives lowest $\mathcal{E}$

C

(25) Ni^{2+}: $3d^8$ O_h high spin

$\uparrow\downarrow\uparrow\uparrow\uparrow$ t_{2g} $\uparrow\uparrow$ e_g (2)

Ru^{3+}: $4d^5$ O_h low spin

$\uparrow\downarrow\uparrow\downarrow\uparrow$ t_{2g} $--$ e_g (1)

Fe^{3+}: $3d^5$ high spin (5)

Cu^{2+}: $3d^9$ $\Rightarrow$ (1)

C