Answers- Additional Probs Ch. 20

1. Find $[Ag^+]$ in saturated Ag_2CrO_4, then calc E_{cell}.

$$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+ + CrO_4^{2-} \qquad K_{sp} = 1.1 \times 10^{-12}$$

some	0	0
$-x$	$+2x$	$+x$
some $-x$	$2x$	x

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2x)^2(x) = 4x^3 = 1.1 \times 10^{-12}$$

$$x = \sqrt[3]{\frac{1.1 \times 10^{-12}}{4}} = 6.\bar{5}0 \times 10^{-5}\ M$$

$$[Ag^+] = 2x = 1.\bar{3}0 \times 10^{-4}\ M\ Ag^+ \text{ in cell.}$$

Find overall equation and E°, then use Nernst.

anode // cathode so Cu is anode (ox), Ag is cathode (red)

$Cu \rightarrow Cu^{2+} + 2e^-$ $\quad E^\circ = -0.3419\ V$ ← add these two

$e^- + Ag^+ \rightarrow Ag$ $\quad E^\circ = 0.7996\ V$

$2e^- + 2Ag^+ \rightarrow Ag$ $\quad E^\circ = 0.7996\ V$ ←

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + Ag \qquad E^\circ = 0.4577\ V$$

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2} \qquad E = E^\circ - \frac{0.0257\ V}{n} \ln Q$$

$$E = 0.4577\ V - \frac{0.0257\ V}{2} \ln \underbrace{\frac{0.10}{(1.\bar{3}0 \times 10^{-4})^2}}_{5.\bar{9}17 \times 10^6}$$

$= 15.5\bar{9}34$

$E = 0.257\ V$

~~$E = 0.1\bar{9}8\ V$~~

~~$-0.25\bar{9}55$~~

-0.20037

~~$E = 0.198\ V$~~

anode cathode

2. $Ag, AgCl_{(s)} \mid Cl^-(x\ M) \parallel Cu^{2+}(0.25M) \mid Cu_{(s)}$

what $[Cl^-]$ to have $E = 0.100V$?

anode contains AgCl in equilibrium with Cl^-. It will contain a small $[Ag^+]$.

Non-std conditions, so use Nernst. First, we need overall rxn and E°. Here, Ag is ~~an~~ anode, so it must be oxidized.

$2(Ag \rightarrow Ag^+ + e^-)$ $\quad E^\circ = -0.7996\ V$

$Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E^\circ = 0.3419\ V$

$2Ag + Cu^{2+} \rightarrow 2Ag^+ + Cu$ $\quad E^\circ = -0.4577\ V$

this is nonspontaneous under standard conditions. Under <u>these</u> conditions, it's spontaneous. $[Ag^+]$ in equilibrium with AgCl will be <u>very</u> low. $[Ag^+]$ is a product - lowering [product] makes rxn more favorable. In this case, it changes rxn from nonspontaneous to spontaneous.

$Q = \dfrac{[Ag^+]^2}{[Cu^{2+}]}$ use Nernst to calc $[Ag^+]$. Then use other info (Ksp) to calc. $[Cl^-]$ in cell.

$E = E^\circ - \dfrac{0.0257\ V}{n} \ln Q$

$0.100\ V = -0.4577\ V - \dfrac{0.0257\ V}{2} \ln Q$

$+0.4577 \quad +0.4577$

$0.55\bar{7}7\ V = -\dfrac{0.0257\ V}{2} \ln Q$

$\dfrac{2(0.55\bar{7}7\ V)}{-0.0257\ V} = \ln Q = -43.\bar{4}01 \qquad Q = e^{-43.\bar{4}01} = 1.\bar{4}17 \times 10^{-19}$

$Q = \dfrac{[Ag^+]^2}{[Cu^{2+}]} \qquad [Ag^+] = \sqrt{Q[Cu^{2+}]} = \sqrt{(1.\bar{4}17 \times 10^{-19})(0.25)} = 1.\bar{8}82 \times 10^{-10}\ M$ Ag^+

$K_{sp} = [Ag^+][Cl^-]$ $\qquad AgCl \rightleftharpoons Ag^+ + Cl^-$ $\qquad x = 1.\bar{8}82 \times 10^{-10}\ M$

some

$-x \quad +x \quad +x$

$x \quad Y+x$

$[Cl^-] = \dfrac{K_{sp}}{[Ag^+]}$

$[Cl^-] = \dfrac{1.8 \times 10^{-10}}{1.882 \times 10^{-10}}$

neglect x

$[Cl^-] = 0.\bar{9}56\ M$

$[Cl^-] = 1\ M$

IGNORE

5 a. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\quad \Delta G^\circ = -nFE^\circ$

$\frac{\Delta H^\circ - T\Delta S^\circ}{-nF} = \frac{-nFE^\circ}{-nF}$

$E^\circ = \frac{-\Delta H^\circ}{nF} + \frac{T\Delta S^\circ}{nF}$ OR $E^\circ = \frac{\Delta H^\circ - T\Delta S^\circ}{-nF}$

b. To make a battery w/ voltage that doesn't change much w/ T: choose a rxn with a small value of ΔS°. This minimizes the contribution of the temperature term ($\frac{T\Delta S^\circ}{nF}$). If ΔS° is smaller, a change in temp won't change the value of E° much. * small magnitude of ΔS° * Having a large value of n would also help.

3. $Ag_{(s)} \mid Ag^+ (aq, sat\ AgBr) \parallel Ag (aq, 0.100M) \mid Ag_{(s)}$

anode cathode

$E = 0.305V$ Conc. cell

$Ag \longrightarrow Ag^+ + e^-$ ox, an

$Ag^+ + e^- \longrightarrow Ag$ red, cat

$Ag + Ag^+_{cat} \rightarrow Ag + Ag^+_{an}$

$Q = \frac{[Ag^+]_{an}}{[Ag^+]_{cat}}$ ← dilute / ← conc. $\qquad E^\circ = 0$

$E = E^\circ - \frac{0.0257}{n} \ln Q$

$0.305V = 0 - \frac{0.0257}{1} \ln Q$

$\frac{0.305V}{-0.0257V} = \ln Q = -11.8677 \qquad Q = e^{-11.8677} = 7.013 \times 10^{-6}$

$Q = \frac{[Ag^+]_{an}}{0.100M} \qquad [Ag^+]_{an} = Q(0.100M) = 7.013 \times 10^{-7} M$

b. $K_{sp} = [Ag^+][Br^-]$ $\quad K_{sp} = x^2$

$AgBr \rightleftharpoons Ag^+ + Br^-$

same 0 0

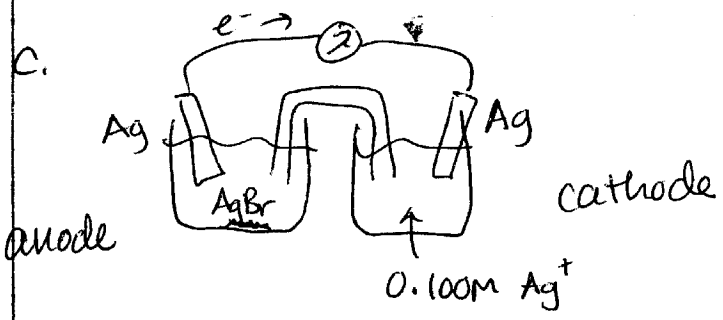
$-x \quad +x \quad +x$

$x \quad x$

$x = 7.013 \times 10^{-7} M$

$x^2 = 5 \times 10^{-13} = K_{sp}$

3 c.



4. $Pb | PbSO_{4(s)}, SO_4^{2-}(0.10\,M) \| H_3O^+(1.0\,M) | H_2(1.0\,atm) | Pt_{(s)}$

anode cathode

$K_{sp}\ PbSO_4 = 1.7 \times 10^{-8}$

$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$

some	0	0.10 M
−x	+x	+x
some − x	x	0.10 + x

negligible

$K_{sp} = [Pb^{2+}][SO_4^{2-}]$

$= (x)(0.10)$

$x = [Pb^{2+}] = \frac{K_{sp}}{[0.10]} = \frac{1.7 \times 10^{-8}}{0.10}$

$[Pb^{2+}] = 1.7 \times 10^{-7} M$

In Nernst eq - need overall rxn and E°. Pb is anode - it's oxidized

$Pb \rightarrow Pb^{2+} + 2e^- \quad E^\circ = +0.1262\ V$

$2H^+ + 2e^- \rightarrow H_2 \quad E^\circ = 0\ V$

$Pb + 2H^+ \rightarrow Pb^{2+} + H_2 \quad E^\circ = +0.1262\ V$

$Q = \frac{[Pb^{2+}]P_{H_2}}{[H^+]^2}$

$E = E^\circ - \frac{0.0257\,V}{n} \ln Q = 0.1262\ V - \frac{0.0257\,V}{2} \ln \frac{(1.7 \times 10^{-7})(1.0)}{(1.0)^2}$

$\ln \frac{(1.7 \times 10^{-7})(1.0)}{(1.0)^2} = -15.587$

$-\frac{0.0257\,V}{2} \times -15.587 = +0.2003\ V$

$E = 0.326499 = \boxed{0.326\,V}$

0.1262 V

(5)

5. Ag - cathode - reduction $\times 2$ $(Ag^+ + e^- \rightarrow Ag)$ $E^\circ = +0.7996\ V$

SHE - anode - ox $H_{2(g)} + 2H_2O \rightarrow 2H_3O^+ + 2e^-$ $E^\circ = 0\ V$

overall: $2Ag^+ + H_2 + 2H_2O \rightarrow 2Ag + 2H_3O^+$ $E^\circ = +0.7996\ V$

$$Q = \frac{[H_3O^+]^2}{[Ag^+]^2 P_{H_2}} \qquad E = E^\circ - \frac{0.0257\ V}{n} \ln Q$$

$$0.45V = 0.7996V - \frac{0.0257V}{2} \ln Q$$

$$-0.7996 \quad -0.7996$$

$$-0.3496\ V = -\frac{0.0257}{2} \ln Q$$

$$\frac{(-0.3496V)(2)}{(-0.0257\ V)} = 27.206 = \ln Q$$

$$Q = e^{27.206} = 6.539 \times 10^{11} \quad \text{no sig figs}$$

SHE so $P_{H_2} = 1\ atm$, $[H_3O^+] = 1\ M$

$$Q = \frac{(1)^2}{[Ag^+]^2(1)} \qquad [Ag^+] = \sqrt{\frac{1}{Q}} = \sqrt{\frac{1}{6.539 \times 10^{11}}}$$

$[Ag^+] = 1.237 \times 10^{-6}\ M$ (no sf)

$AgSCN \rightleftharpoons$	Ag^+	$+ SCN^-$
some	0	0.10
$-x$	$+x$	$+x$
	x	$0.10 + x$

$0.10 + x$ ← negligible

$$K_{sp} = (x)(0.10) = (1.237 \times 10^{-6})(0.10) = 1.237 \times 10^{-7} \text{ no sf}$$

$$K_{sp} = 10^{-7}$$