Chp. 2 HW
7750-002

E° (NHE

2.1 ⓐ $H_2O + e^- \rightleftharpoons \frac{1}{2} H_2 + {}^-OH$ -0.8277

$-(H^+ + e^- \rightleftharpoons \frac{1}{2} H_2)$ 0.000

See piece

$H_2O \rightleftharpoons H^+ + {}^-OH$ -0.8277

E is $\ominus$ → Electrolytic.

Thus, the anode must be positive.

So, $H_2O + e^- \rightleftharpoons \frac{1}{2} H_2 + {}^-OH$ is $\ominus$.

$Pt / H_2 (a=1) / HCl (a=1) // NaOH (a=1) / H_{2(a=1)} / P$

ⓑ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ 1.229

$-8(H^+ + e^- \rightleftharpoons \frac{1}{2} H_2)$ 0.000

$2H_2 + O_2 \rightleftharpoons 2H_2O$ $1.229V$

Galvanic → anode $\ominus$.

H^+/H_2 electrode is $\ominus$.

$Pt / H_2 (a=1) / H^+_{(a=1)} / O_2 (a=1) / Pt$

or

$Pt / H_2 (a=1) / H^+_{(a=1)} // H^+_{(a=1)} / O_2 (a=1) / Pt.$

(c.) Car battery.

$\underline{PbSO_4} + 2e \rightleftharpoons Pb^\circ + SO_4^{2-}$ −0.356

$-(PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons \underline{PbSO_4} + 2H_2O$ 1.685)

$2PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + Pb^\circ + 4H^+ + 2SO_4^{2-}$

$E^\circ_{cell} = -2.041$

Electrolytic, so anode is ⊕.

Pb/PbSO4 is ⊖

$Pb/PbO_2/PbSO_4/H^+(a=1), SO_4^{2-}(a=1)//PbSO_4/Pb$

(d.) $TMPD^{\dot{+}} + e^- \rightleftharpoons TMPD^\circ$ 0.21V vs. SC

(in 0.1M TBAP/CH_3CN) (1mM of each)

$-(An^\circ + e^- \rightleftharpoons An^{\dot{-}}$ −1.92V)

(in 0.1M TBAP/CH_3CN) (1mM of each)

$TMPD^{\dot{+}} + An^{\dot{-}} \rightleftharpoons An^\circ + TMPD^\circ$ 2.13

Galvanic, so anode is ⊖

$An^{\dot{-}}/An^\circ$ is ⊖.

$Pt/An^{\dot{-}}$(1mM), An°(1mM) in CH_3CN, 0.1M TBAP // $TMPD^{\dot{+}}$(1mM), $TMPD^\circ$(1mM) in CH_3CN, 0.1M TBAP / Pt.

ⓔ

$$\overset{\curvearrowright 1mM}{BQ} + 2H^+ + 2e^- \rightleftharpoons \underset{\to 1mM}{H_2Q} \qquad 0.6992$$

$$-2(\underset{\to 1mM}{Ce^{4+}} + 1e^- \rightleftharpoons \underset{\to 1mM}{Ce^{3+}} \qquad 1.44)$$

$$H^+ + BQ + 2Ce^{3+} \rightleftharpoons 2Ce^{4+} + H_2Q \quad -0.74$$

Electrolytic, so anode is $\oplus$.

$Ce^{3+/4+}$ is $\oplus$, BQ/H_2Q is $\ominus$.

$Pt / Ce^{4+}(1mM), Ce^{3+}(1mM), H_2SO_4 (1M) //$

$BQ (1mM), H_2Q(1mM), H^+(a=1), SO_4^{2-} / Pt$

You could use other acids as well.

ⓕ

$$Ag^+ + e^- \rightleftharpoons \underline{Ag^\circ} \qquad 0.7996$$

$$-(\underline{AgI} + e^- \rightleftharpoons \underline{Ag^\circ} + I^- \quad -0.1519)$$

$$Ag^+ + I^- \rightleftharpoons AgI \qquad 0.9515$$

Galvanic (as expected for this pptin)

so anode is $\ominus$,

AgI/Ag° is $\ominus$.

$Ag / AgI / I^-(a=1) // Ag^+(a=1) / Ag.$

2-4

ⓗ $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}\ (1mM)$ $+0.770$
(in 1M HCl)

$$-\left(Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-} \quad +0.69\right)$$

$$Fe^{3+} + Fe(CN)_6^{4-} \rightleftharpoons Fe^{2+} + Fe(CN)_6^{3-}$$

$E^\circ_{cell} = 0.08V$

Galvanic, anode $\ominus$, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ $\ominus$.

$Pt/Fe(CN)_6^{4-}(1mM),\ Fe(CN)_6^{3-}(1mM),\ \underset{\text{or HCl}}{H_2SO_4}(a=1)\,//$
$Fe^{3+}(1mM),\ Fe^{2+}(1mM),\ HCl\ (a=1)/\,Pt$

ⓘ $Cu^{2+} + 2e^- \rightleftharpoons \underline{Cu^0}$ 0.3402

$$-\left(Pb^{2+} + 2e^- \rightleftharpoons \underline{Pb^0} \quad -0.1263\right)$$

$$Cu^{2+} + Pb^0 \rightleftharpoons \underline{Cu^0} + Pb^{2+} \quad 0.4665V$$

Galvanic, so anode $\ominus$,
Pb^0/Pb^{2+} is $\ominus$.

$Pb/Pb^{2+}(a=1)\ //\ Cu^{2+}(a=1)\ /\ Cu$

↑ NO_3^- salt OK

↑ NO_3^- or SO_4^{2-} OK.

(f) 2-3

DMF 0.1M TBAP — $\text{An} + e^- \rightleftharpoons \text{An}^{\overline{\cdot}}$ −1.92 V (SCE)

DMF 0.1M TBAP — $\text{BQ} + e^- \rightleftharpoons \text{BQ}^{\overline{\cdot}}$ −0.54 V (SCE)

$\text{BQ} + \text{An}^{\overline{\cdot}} \rightleftharpoons \text{BQ}^{\overline{\cdot}} + \text{An}$ 1.38

Galvanic, anode $\ominus$,

$\text{An}^{\overline{\cdot}}/\text{An}^{\cdot}$ is $\ominus$.

Pt/An (1mM), $\text{An}^{\overline{\cdot}}$ (1mM) in DMF, 0.1M TBAP //

$\text{BQ}^{\overline{\cdot}}$ (1mM), BQ (1mM) in DMF, 0.1M TBAP / Pt.

<u>Note:</u> must use aprotic solvents
to prevent

$\text{Solv.–H} + \text{An}^{\overline{\cdot}} \longrightarrow \text{An–H} + \text{Solv.}^{\cdot}$

H· atom abstraction.

Same for BQ.

2.3 $$2\left(1e^- + Na^+ \overset{Hg}{\rightleftharpoons} Na(Hg)\right) \qquad E^\circ = ?$$

$$-\left(Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad 1.360\right)$$

$$2Cl^- + 2Na^+ \rightleftharpoons 2\,\underline{Na(Hg)} + Cl_2\uparrow$$

$$E^\circ = ? - 1.360$$

Well, we know

$$e^- + Na^+ \rightleftharpoons Na^\circ \qquad E^\circ = -2.711\,V$$

and we know

$$Na^\circ \rightleftharpoons Na(Hg) \qquad \Delta G^\circ = -170\,KJ$$

and $\Delta G^\circ_{Amal.} = -nFE^\circ$ $\quad E^\circ_{Amal.} = \dfrac{-(-170\,KJ)}{(1)(96487\frac{C}{e})}$

$$E^\circ_{Amal.} = +0.88\,V$$

So

$$e^- + Na^+ \rightleftharpoons Na^\circ \qquad -2.711$$

$$Na^\circ \rightleftharpoons Na(Hg) \qquad +0.88\,V$$

$$Na^+ + e^- \rightleftharpoons Na(Hg) \qquad -1.83\,V$$

Thus, for our net rxn. above,

$$\boxed{E^\circ_{Net} = -3.15\,V}$$

Rxn. is certainly NOT spontaneous.

But we forgot:

$$2\,Na(Hg) + 2\,H_2O \rightleftarrows NaOH + H_2.$$

So, we get energy from this!

The proposed competing rxn would be reduction of water:

$$2\,H_2O + 2e \rightleftarrows H_2 + 2\,\bar{O}H.$$

But this is Kinetically VERY slow!

The cell is the brine/Hg cell used to make Cl_2, $NaOH$, + H_2 from NaCl solutions.

2.4 Anode Cathode

(a) Ag/AgCl/K$^+$, Cl$^-$ (1M)//Hg$_2$Cl$_2$/Hg

$E^{\circ\prime}_{NHE}$ (V)

$-2(\underline{AgCl} + e^- \longleftrightarrow Ag^\circ + Cl^-)$ +0.2223

$+(\underline{Hg_2Cl_2} + 2e^- \longleftrightarrow 2Hg^\circ + 2Cl^-)$ +0.2682

$\underline{Hg_2Cl_2} + 2Ag^\circ \longleftrightarrow 2Ag^\circ + \underline{AgCl}$ +0.0459

Spontaneous due to $-\Delta G$

(b) Pt/Fe^{3+}(0.01M), Fe^{2+}(0.1M), HCl(1M)//
Cu^{2+}(0.1M), HCl(1M)/Cu

$\underline{E_{(NHE)}}$

$-2(Fe^{3+} + e^- \longleftrightarrow Fe^{2+})$ E = +0.70 + 0.0591 (−1) = +0.64 V

$Cu^{2+} + 2e^- \longleftrightarrow \underline{Cu^\circ}$ E = +0.34 + $\frac{0.0591}{2}$ (−1) = +0.310 V

$2Fe^{2+} + Cu^{2+} \longleftrightarrow \underline{Cu^\circ} + Fe^{3+}$

E_{cell} = −0.33 V vs NHE

Not Spontaneous

2.4 (c)

Pt/H_2 (1 atm)/H^+, Cl^- (0.1M)//H^+, Cl^- (0.1M)/O_2 (0.2 atm) Pt

$\underline{E}$

$-2(2H^+ + 2e^- \longleftrightarrow H_2)$ $E = 0.000 + 0.0591\cdot(-1)$
$E = -0.0591\,V$

$O_2 + 4H^+ + 4e^- \longleftrightarrow 2H_2O$ $E = 1.229 + \frac{0.0591}{4}\log(0.2\cdot 0.1)$
$E = 1.160\,V$

$2H_2 + O_2 \longleftrightarrow 2H_2O$ $E = 1.219\,V$ vs NHE

$\boxed{\text{Spontaneous}}$

(d.) Pt/H_2 (1 atm)/Na^+, OH^- (0.1M)//Na^+, OH^- (0.1M)/ O_2 (0.2 atm)/Pt

$-2(2H_2O + 2e^- \longleftrightarrow H_2\uparrow + 2OH^-)$ $E = -0.828 + 0.0591\cdot\log(0.1\cdot 1)$
$E = -0.887\,V$

$O_2\uparrow + 4e^- + 2H_2O \longleftrightarrow 4OH^-$ $E = 0.401 + \frac{0.0591}{4}\cdot\log\frac{(0.2)}{(0.1)}$
$E = 0.401 + 0.049 = 0.450\,V$

$2H_2\uparrow + O_2\uparrow \longleftrightarrow 2H_2O$ $E = 1.337\,V$ vs NHE

$\boxed{\text{Spontaneous!}}$

2.4

(e) $Ag/AgCl/K^+, Cl^-\ (1M)//K^+, Cl^-\ (0.1M)/AgCl/Ag$

$-\left(\underline{AgCl} + e^- \longleftrightarrow Ag^0 + Cl^-\right)$ $E = 0.2223 + \frac{0.059}{1}\log(1)$

$E = 0.2223V$

$\underline{AgCl} + e^- \longleftrightarrow Ag^0 + Cl^-$

$E = 0.2223 + \frac{0.059}{1}\cancel{\log}\left(\frac{1}{0.1}\right)$

$E = 0.2814V$

$Cl^-_{(1M)} \rightleftarrows Cl^-_{(0.1M)}$ $E = 0.059\ V$

$\boxed{\text{Spontaneous}}$

(f) $Pt/Ce^{3+}(0.01M), Ce^{4+}(0.1M), H_2SO_4(1M)//$
$Fe^{2+}(0.01M), Fe^{3+}(0.1M), HCl(1M)/Pt$

$-\left(Ce^{4+} + e^- \longleftrightarrow Ce^{3+}\right)$ $E = 1.44 + \frac{0.059}{1}\log\frac{0.1M}{0.01M}$

$E = 1.78$

$Fe^{3+} + e^- \longleftrightarrow Fe^{2+}$ $E = 0.70 + \frac{0.059}{1}\log\left(\frac{0.1M}{0.01M}\right)$

$E = 0.76$

$Ce^{3+} + Fe^{3+} \longleftrightarrow Ce^{4+} + Fe^{2+}$ $E = 0.9– V$

$\boxed{\text{Not Spontaneous}}$

2.6

Net: $\underline{PbSO_4} \overset{K_{sp}}{\rightleftharpoons} Pb^{2+} + SO_4^{2-}$

$$-\left(Pb^{2+} + 2e^- \rightleftharpoons \underline{Pb^\circ}\right)$$

$$\left(\underline{PbSO_4} + 2e^- \rightleftharpoons \underline{Pb^\circ} + SO_4^{=}\right)$$

$$\underline{PbSO_4} \overset{K_{sp}}{\rightleftharpoons} Pb^{2+} + SO_4^{2-} \quad E^\circ_{rxn}$$

K_{sp} is defined when $a = 1$ for all species:

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

$$\Delta G^\circ = \ominus nF E^\circ_{rxn} = \ominus RT \ln K_{sp}$$

so, $K_{sp} = \exp\left(\frac{nF E^\circ_{rxn}}{RT}\right)$

$E^\circ_{rxn} = -0.2297$ V, as it should be for an unfavorable rxn.!
We predict then that K_{sp} will be tremendously small.

$$\boxed{K_{sp} = 1.70 \times 10^{-8} \text{ at } RT}$$