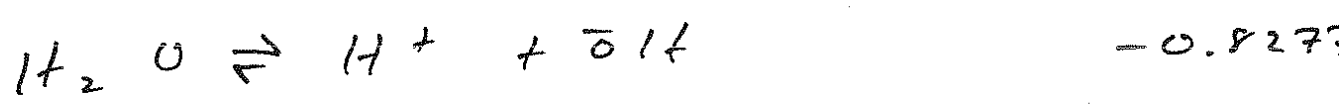


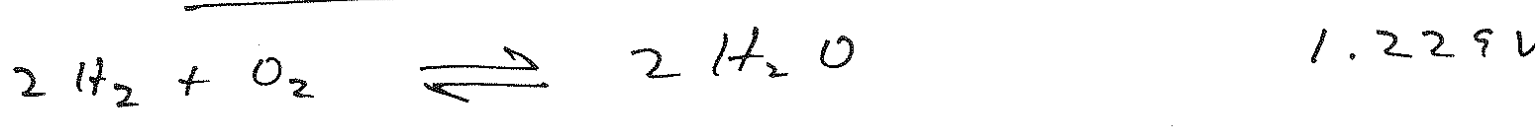
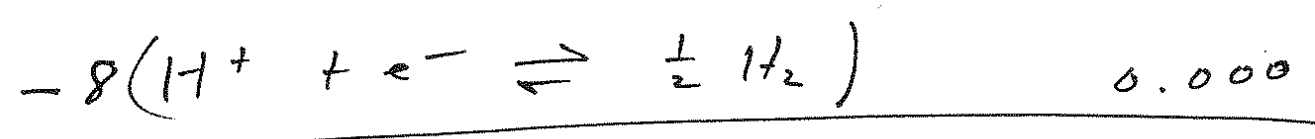
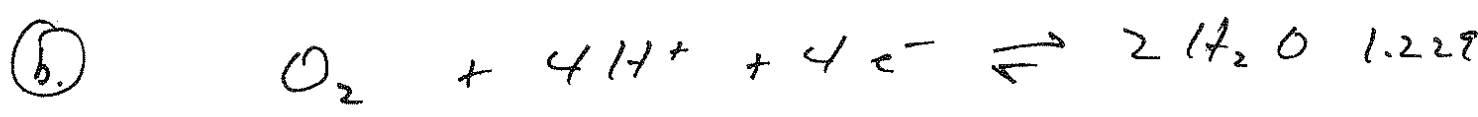
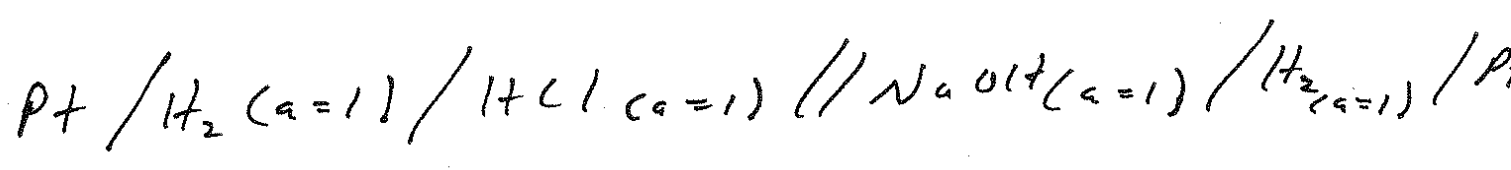
See piece



E is $\ominus \rightarrow$ Electrolytic.

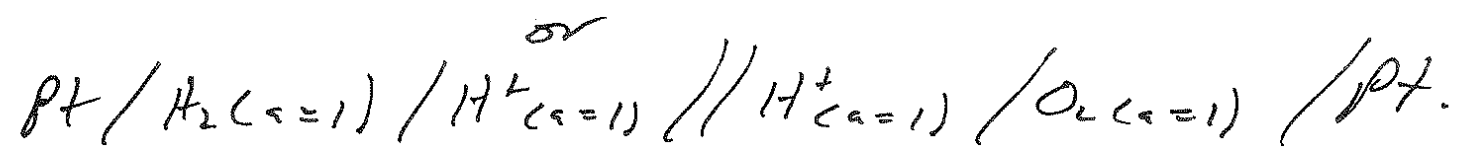
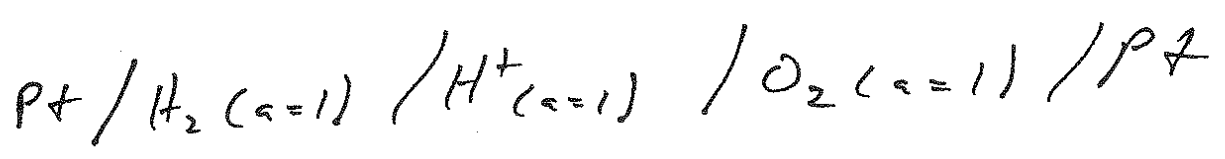
Thus, the anode must be positive.

So, $\text{H}_2\text{O} + e^- \rightleftharpoons \frac{1}{2}\text{H}_2 + \text{OH}^-$ is \ominus .



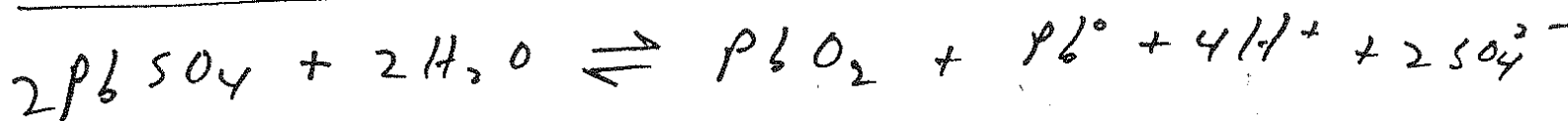
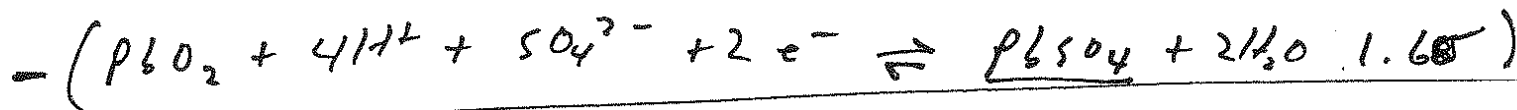
Galvanic \rightarrow anode \ominus .

H^+ / H_2 electrode is \ominus .



② Carbonyl.

2-2

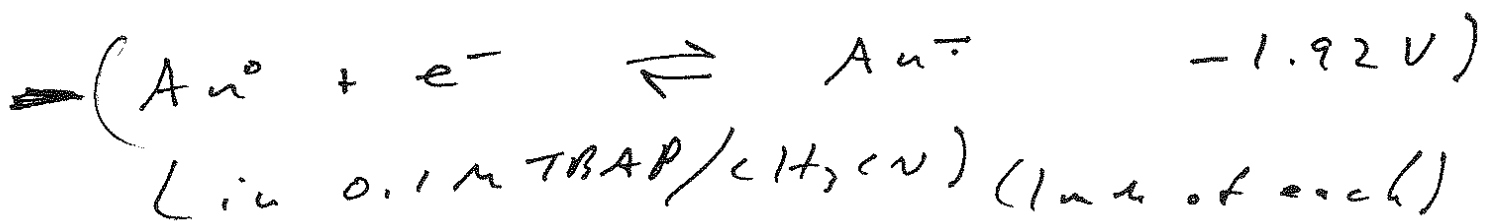
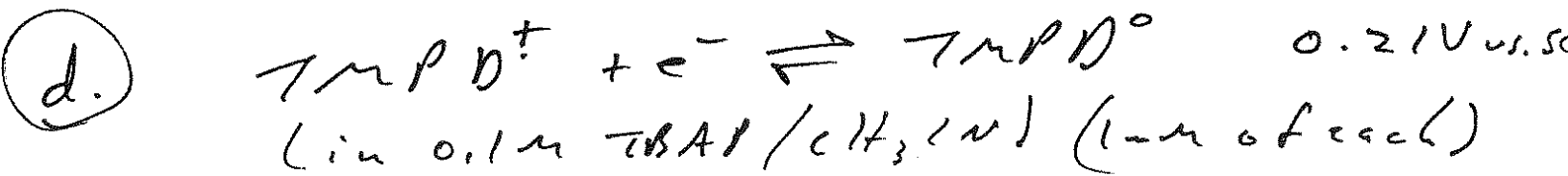


$$E_{\text{cell}}^{\circ} = -2.041$$

Electrolyte, so anode is ⊕.

Pb/PbSO₄ is ⊖

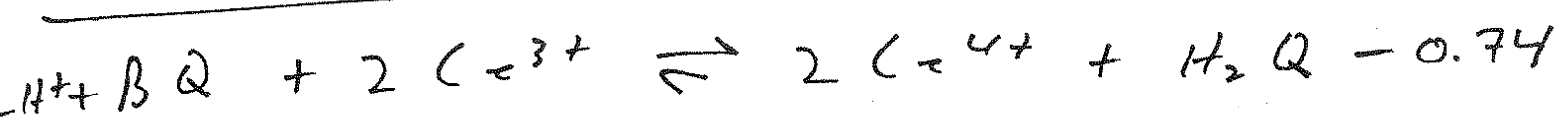
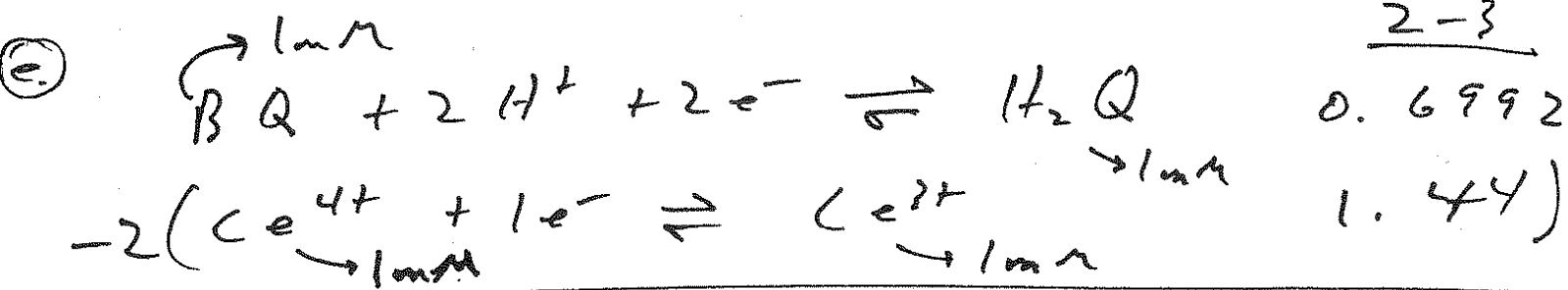
Pb/PbO₂/PbSO₄ / H⁺ (c=1), SO₄²⁻ (c=1) / PbSO₄/Pb



Galvanic, so anode is ⊖

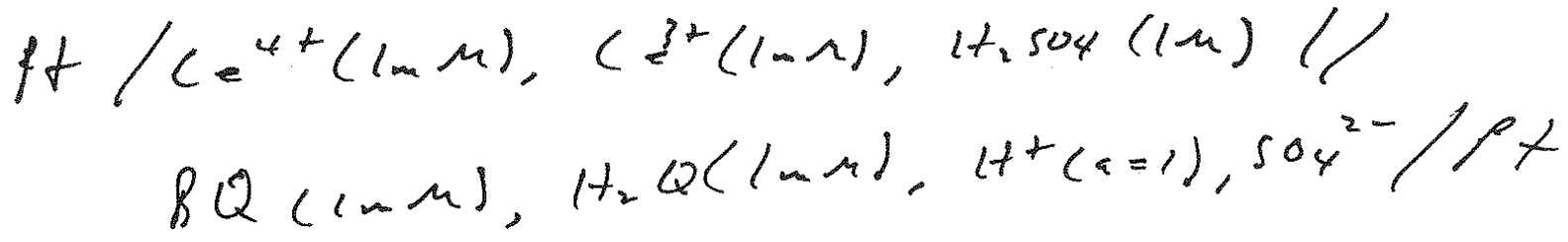
Au⁻/Au⁰ is ⊖.

PT/Au⁻ (1 mM), Au⁰ (1 mM) in CH₃CN, 0.1 M TBAP //
TMPD[†] (1 mM), TMPD⁰ (1 mM) in CH₃CN, 0.1 M TBAP / PT.

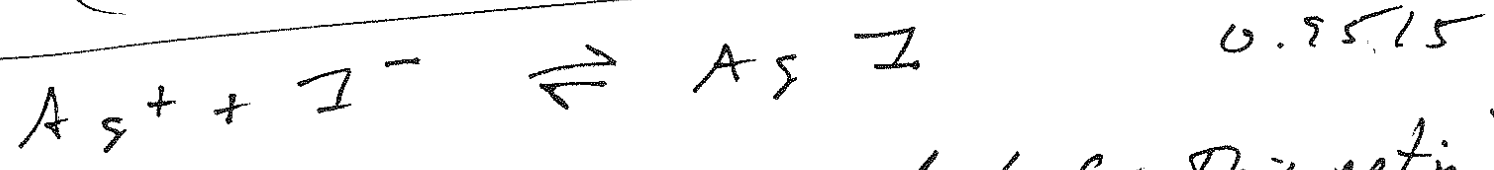
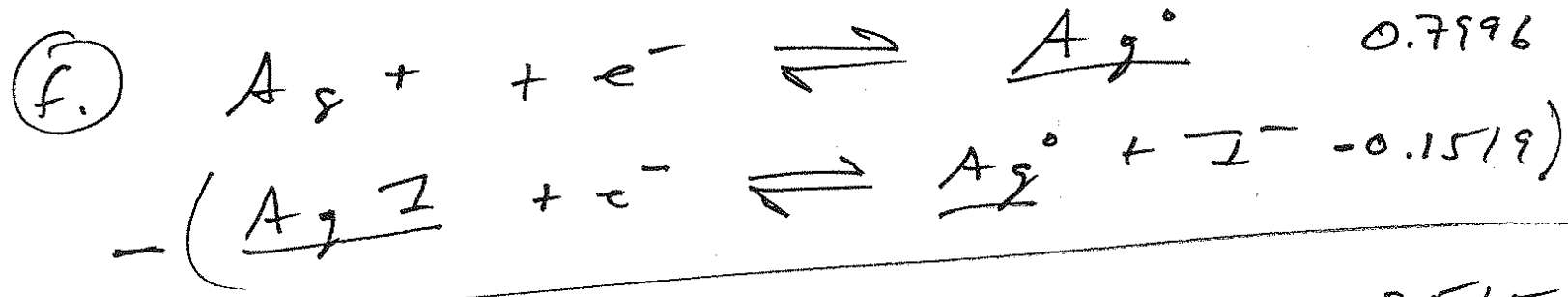


Electrolytic, so anode is \oplus .

$\text{Ce}^{3+}/\text{Ce}^{4+}$ is \oplus , $\text{Br}_2/\text{H}_2\text{O}$ is \ominus .



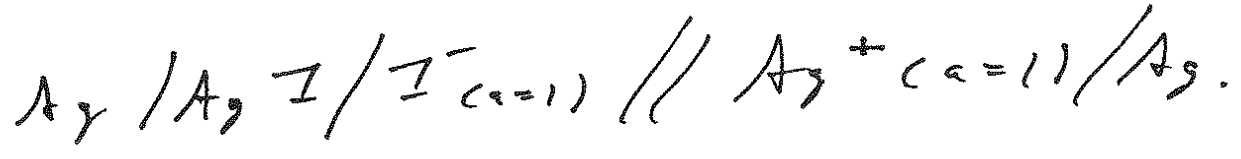
You could use other acids as well.

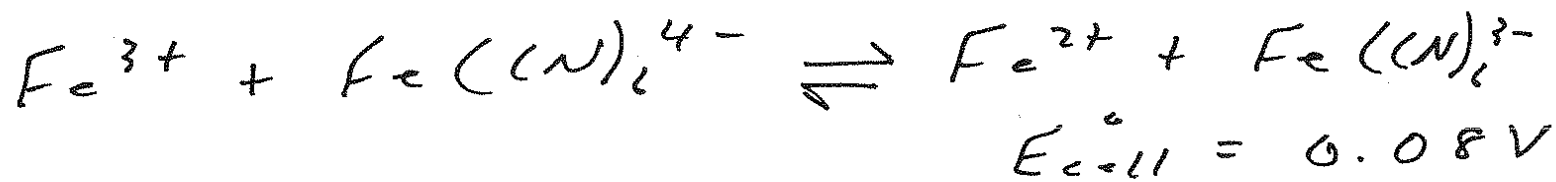
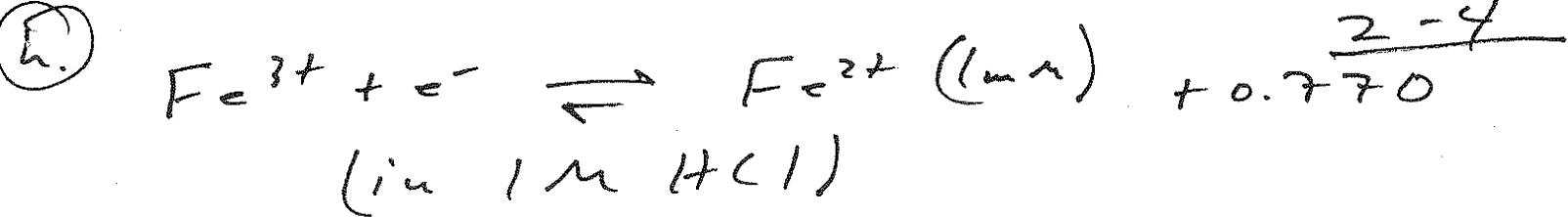


Galvanic (as expected for this problem)

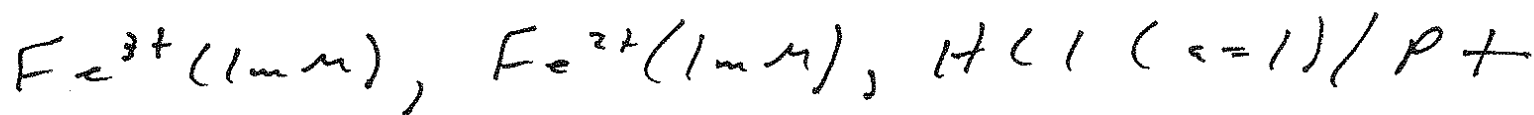
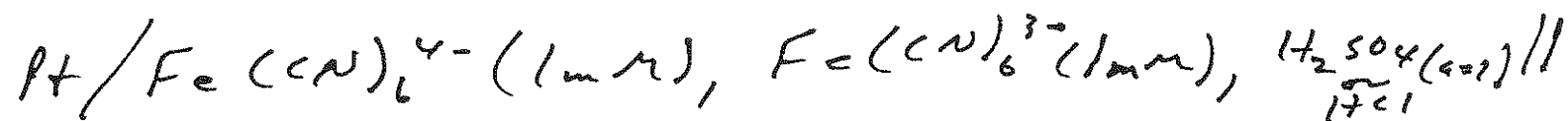
so anode is \ominus ,

AgI/Ag^0 is \ominus .



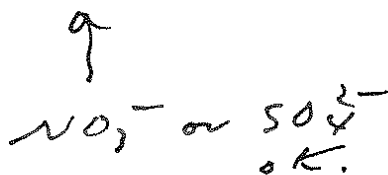
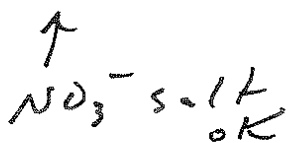


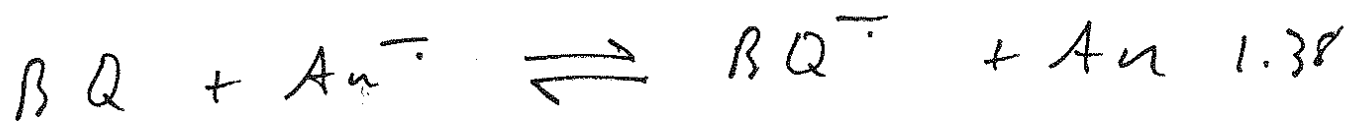
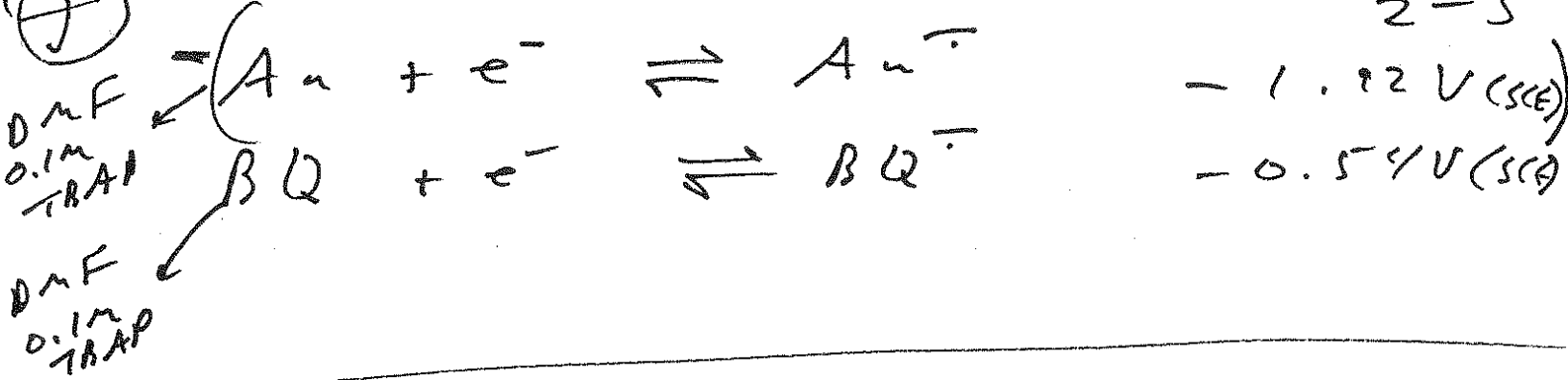
Galvanic, anode \ominus , $Fe(CN)_6^{3-}/Fe(CN)_6^{4-} \ominus$



Galvanic, so anode \ominus ,

Pb°/Pb^{2+} is \ominus .





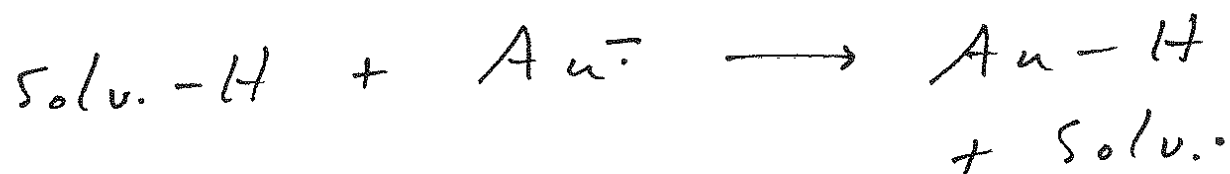
Galvanic, anode \ominus ,

Au^-/Au is \ominus .

Pt/Au (1mM), Au^- (1mM) in DMF, 0.1M TRAP (//

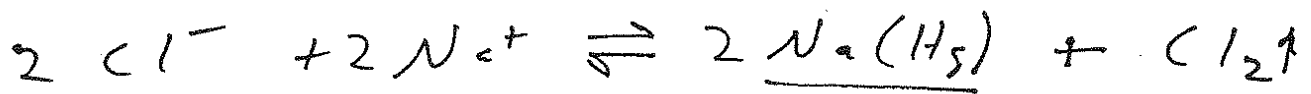
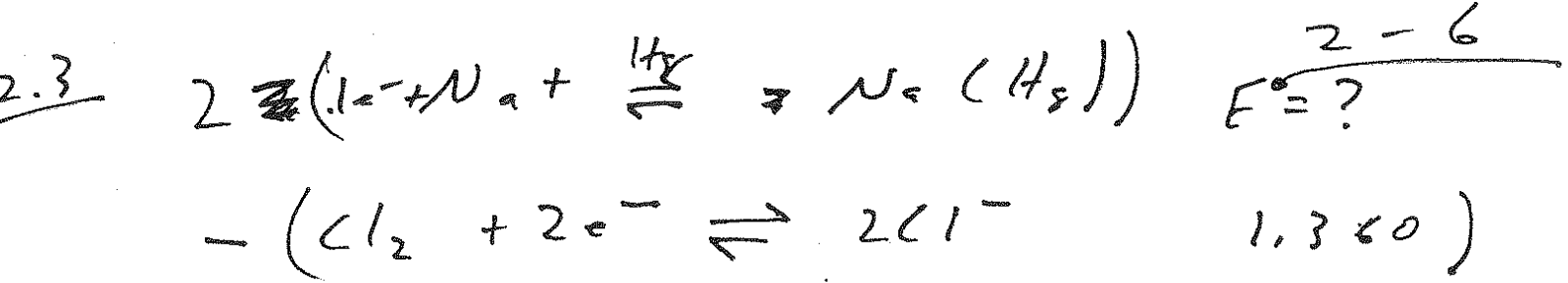
BQ^- (1mM), BQ (1mM) in DMF, 0.1M TRAP // Pt.

Note: must use aprotic solvents
to prevent



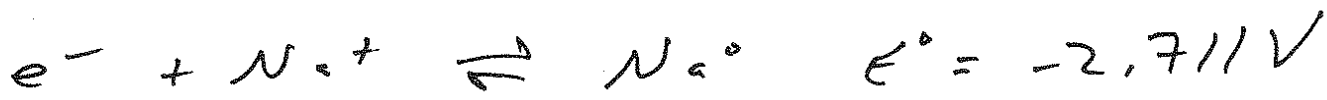
H. atom abstraction.

Same for BQ.

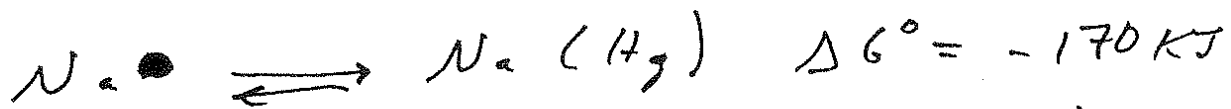


$$E^\circ = ? - 1.360$$

Well, we know



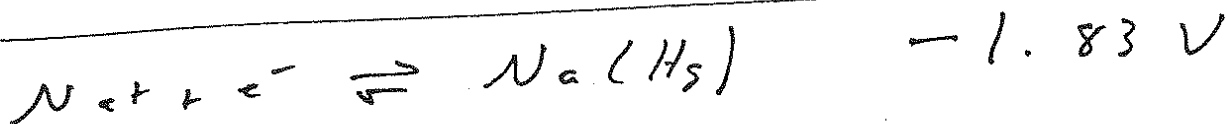
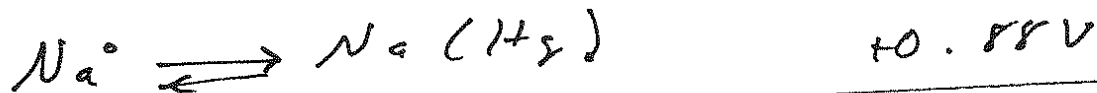
and we know



$$\text{and } \Delta G_{\text{Amd.}}^\circ = -nFE^\circ \quad E_{\text{Amd.}}^\circ = \frac{-(-170 \text{ KJ})}{(1)(96487 \frac{\text{C}}{\text{mol}})}$$

$$E_{\text{Amd.}}^\circ = +0.88 \text{ V}$$

So

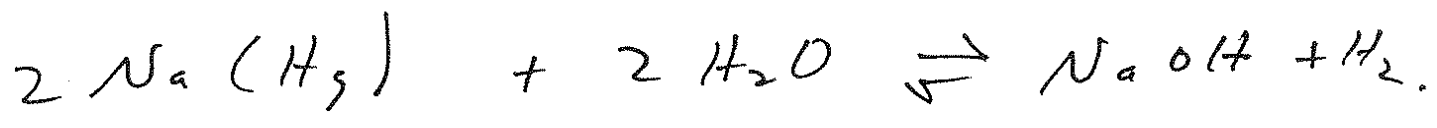


Thus, for our net rxn. above,

$$E_{\text{net}}^\circ = -3.15 \text{ V}$$

Rxn. is certainly NOT 2-7
spontaneous.

But we forget:



So, we get energy from this!

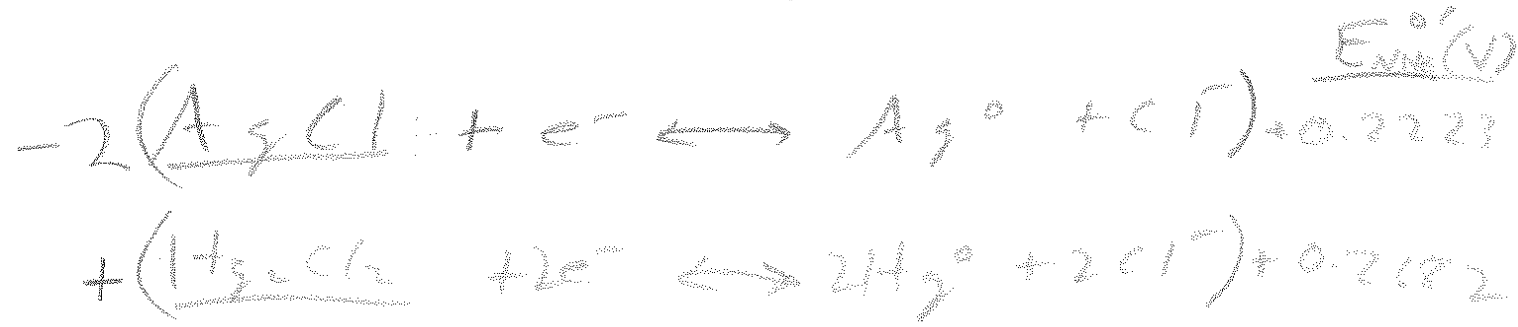
The proposed competing rxn would
be reduction of water:



But this is Kinetically
VERY slow!

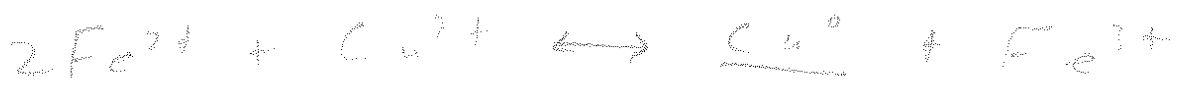
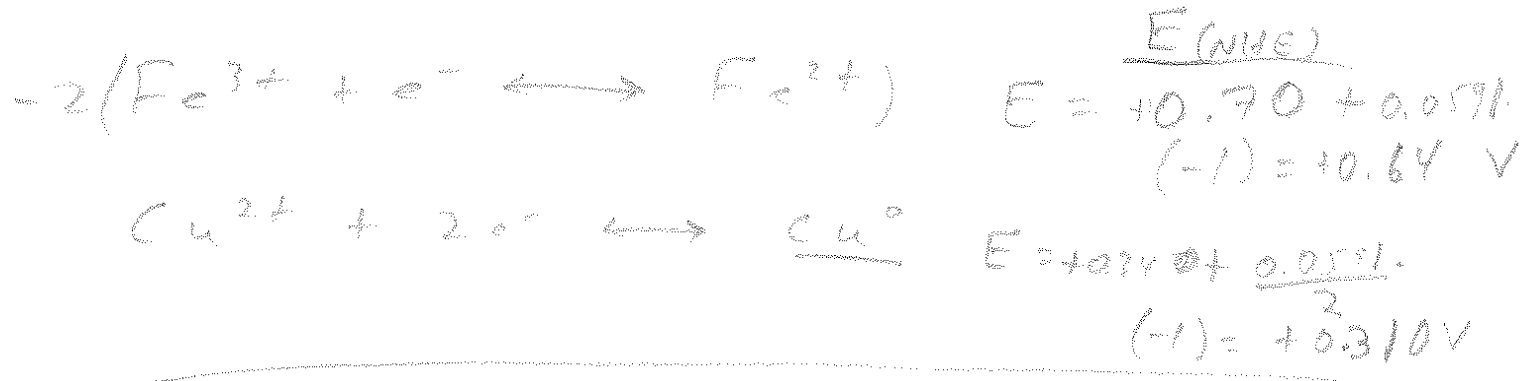
The cell is the brine/Hg cell
used to make Cl_2 , NaOH , + H_2
from NaCl solutions.

2.4 Anode Cathode
 (a) $\text{Ag}/\text{AgCl}/\text{K}^+, \text{Cl}^- (1\text{M})/\text{Hg}_2\text{Cl}_2/\text{Hg}$



Spontaneous due to $-\Delta G$

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



$$E_{\text{cell}} = -0.33 \text{ V vs NHE}$$

Not Spontaneous

2.4 (c)

Pt / H₂ (1 atm) / H⁺, Cl⁻ (0.1 M) // H⁺, Cl⁻ (0.1 M) / O₂ (0.2 atm) / Pt

$$2(2H^+ + 2e^- \leftrightarrow H_2) \quad E = 0.000 + 0.0591 \cdot (-1)$$

$$E = -0.0591 V$$

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

$$E = 1.160 V$$

$$2H_2 + O_2 \leftrightarrow 2H_2O \quad E = 1.219 V \text{ vs NHE}$$

Spontaneous

(d.) Pt / H₂ (1 atm) / NO⁺, OH⁻ (0.1 M) // NO⁺, OH⁻ (0.1 M) / O₂ (0.2 atm) / Pt

$$-2(2H_2O + 2e^- \leftrightarrow H_2 \uparrow + 2OH^-) \quad E = -0.828 + 0.0591 \cdot \log(0.1)$$

$$E = -0.887 V$$

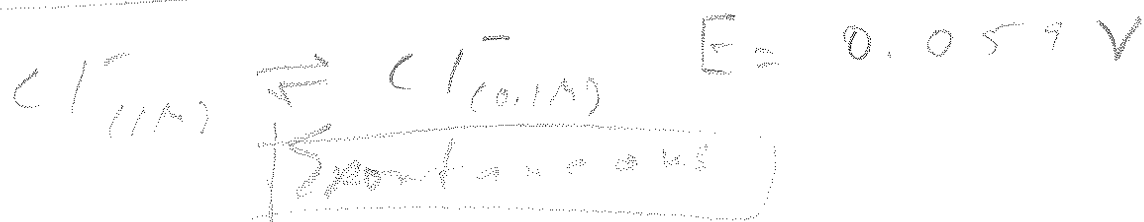
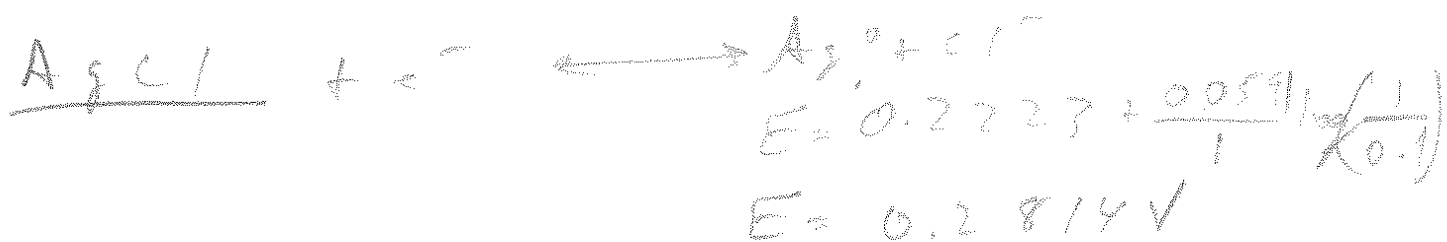
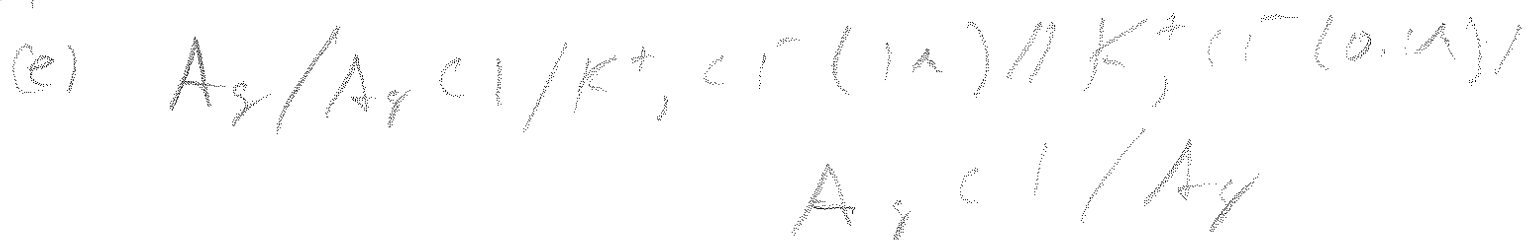
$$O_2 + 4e^- + 2H_2O \leftrightarrow 4OH^- \quad E = 0.401 + \frac{0.0591}{4} \cdot \log\left(\frac{0.2}{0.1^4}\right)$$

$$E = 0.401 + 0.049 = 0.450 V$$

$$2H_2 \uparrow + O_2 \uparrow \leftrightarrow 2H_2O \quad E = 1.337 V \text{ vs NHE}$$

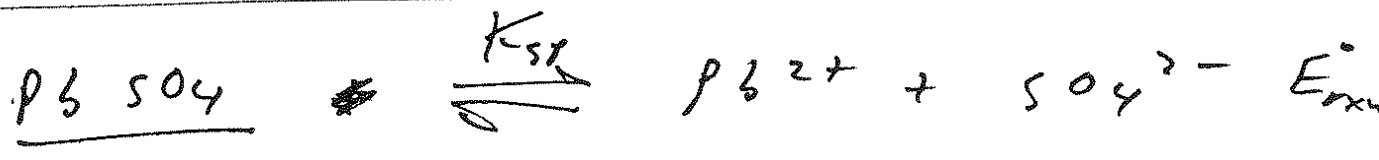
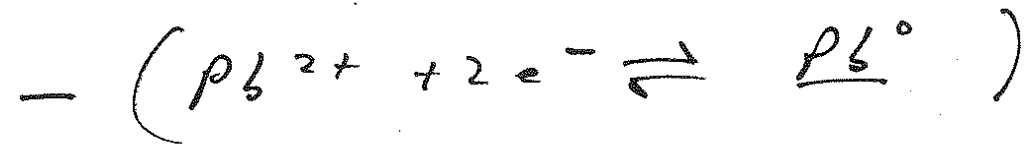
Spontaneous!

2.4



Not Spontaneous

2.6



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

$$K_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

$$\Delta G^{\circ} = -nF E_{rxn} = -RT \ln K_{sp}$$

$$\text{so, } K_{sp} = \exp\left(\frac{nF E_{rxn}}{RT}\right)$$

$E_{rxn} = -0.2297 \text{ V}$, as it should be
for an unfavorable rxn!

We predict then that K_{sp} will be
tremendously small.

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