Chem 12

HW set 7 - graded part

1. Ch 11, 47c - modified

(i) $\mathcal{E} = 1.84\,V - \frac{0.0257\,V}{3} \ln\left(\frac{(3.1\times10^{-2})^3}{(8.4\times10^{-7})}\right)$

$= 1.81\,V$

(ii) $1.97\,V = 1.84\,V - \frac{0.0257\,V}{3} \ln\left(\frac{[Tl^+]^3}{(1.00\times10^{-4})}\right)$

$[Tl^+] = 2.93\times10^{-4}\,M$

2. Ch 11, 55 - modified

$\mathcal{E} = 0 - \frac{0.0257\,V}{2} \ln\left(\frac{[Ni^{2+}(R)]}{1\,M}\right)$

(i) $[Ni^{2+}] = 2.87\times10^{-2}\,M \Rightarrow \mathcal{E} = .0456\,V$

$= 45.6\,mV$

R electrode is anode — ox of Ni to $Ni^{2+}$ increases $[Ni^{2+}]$

L " " cathode

(ii) $[Ni^{2+}] = 2.43\,M \Rightarrow \mathcal{E} = -.0114\,V$

$= -11.4\,mV$

negative in this case ⇒ cell runs in "reverse" (relative to the direction that defined the set-up of the Nernst eqn - see #55 on the non-graded part)

so R electrode is now the cathode

+ L " " " " anode

(iii) $\mathcal{E} = 0.287\,V \Rightarrow [Ni^{2+}] = 1.94\times10^{-10}\,M$

3. Ch 11, 56 concentration cell

$\mathcal{E} = 0 - \frac{0.0257\,V}{2} \ln\left(\frac{[M^{2+}]}{1\,M}\right)$

$\mathcal{E} = 0.44\,V \Rightarrow [M^{2+}] = 1.29\times10^{-15}\,M$

cont'd ...

3. #58 (cont'd) $MSO_4 \rightleftharpoons M^{2+} + SO_4^{2-}$

made via 0.01 M $M(NO_3)_2$ + 0.01 M $Na_2SO_4$ — ($\uparrow$ $MSO_4$)

$M^{2+}$: calc'd from $\mathcal{E}$

but nearly all the $MSO_4$ precipitates, since the $[M^{2+}]$ is tiny. $[M^{2+}] = [SO_4^{2-}] = 1.29 \times 10^{-15}$ M

so $K_{sp} = [M^{2+}][SO_4^{2-}]$
$= 1.66 \times 10^{-30}$

4. Ch 11 #57

std $H^+/H_2$ electrode so $[H^+] = 1$ M, $P_{H_2} = 1$ atm. & we can leave these out of the Nernst eqn.

$Cu^{2+} \rightarrow Cu \quad \mathcal{E}° = 0.34$ V

a. $\mathcal{E} = 0.34\text{ V} - \frac{0.0257\text{ V}}{2} \ln\left(\frac{1}{[Cu^{2+}]}\right)$

(i.e. $Cu^{2+} + H_2 \rightarrow Cu + 2H^+$

so $\ldots \ln\left(\frac{[H^+]^2}{[Cu^{2+}][H_2]}\right)$ ← 1 std states)

$[Cu^{2+}] = 2.5 \times 10^{-4}$ M

$\Rightarrow \mathcal{E} = 0.23$ V

b. $Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2\,HO^-$

$K_{sp} = [Cu^{2+}][HO^-]^2$

($K_{sp} = 1.6 \times 10^{-19}$, $[HO^-] = 0.10$ M)

$\Rightarrow [Cu^{2+}] = 1.6 \times 10^{-17}$ M

$\Downarrow$

$\mathcal{E} = -0.16$ V

i.e. rxn would run in reverse — $Cu \rightarrow Cu^{2+}$

c. $\mathcal{E} = 0.195$ V

$\Downarrow$

$[Cu^{2+}] = 1.24 \times 10^{-5}$ M

d. Didn't you do something like this in lab?

The eqn $\mathcal{E} = \underbrace{0.34\text{ V}}_{b} - \underbrace{\frac{0.0257\text{ V}}{2}}_{m} \underbrace{\ln\left(\frac{1}{[Cu^{2+}]}\right)}_{x}$

has the form $y = b + m\,x$

so plotting $\mathcal{E}$ vs $\ln(1/[Cu^{2+}])$ will give a line with slope $-\frac{0.0257\text{ V}}{2}$

HW set 7 - S.

5. Ch 10, 20. $S = R \ln \Omega$

table 10.1, p. 415 — I $\Omega = 1$, so $S = 0$

II $\Omega = 4$, so $S = 11.5$ J/mol K

III $\Omega = 6$, so $S = 14.9$ J/mol K

6. Ch 10, 40,

expect: a. 3 → 2 gas molecules $\Delta S°$ negative

b. 2 → 3 " " " positive

c. 3 → 3 hard to tell

a. $\Delta S° = 3\,S°(S_{rh.}) + 2\,S°(H_2O(g)) - 2\,S°(H_2S(g)) - S°(SO_2(g))$

$= 3(32 \text{ J/mol K}) + 2(189 \text{ J/mol K}) - 2(206 \text{ J/mol K}) - (248 \text{ J/mol K})$

$= -186$ J/mol K

b. $\Delta S° = S°(O_2(g)) + 2S°(SO_2(g)) - 2S°(SO_3(g))$

$= (205 \text{ J/mol K}) + 2(248 \text{ J/mol K}) - 2(257 \text{ J/mol K})$

$= +187$ J/mol K

c. $\Delta S° = 2\,S°(Fe(s)) + 3\,S°(H_2O(g)) - S°(Fe_2O_3(s)) - 3\,S°(H_2(g))$

$= 2(27 \text{ J/mol K}) + 3(189 \text{ J/mol K}) - (90 \text{ J/mol K}) - 3(131 \text{ J/mol K})$

$= +138$ J/mol K