Quiz 7
CHEM 311 Fall 2004

In many industrial processes it is important to monitor the redox conditions on-line. This can be accomplished using an indicator electrode to measure the ratio of $[Fe^{3+}]/[Fe^{2+}]$ of the effluent. The indicator electrode is constructed of a Ag/AgCl reference electrode as the anode and a platinum wire as the cathode. Once a day the indictor electrode is calibrated using a series of standards with known $[Fe^{3+}]/[Fe^{2+}]$ ratios (0.00100, 0.0100, 0.100, 1.00, 10.0, 100.0, 1000), and a standard curve is produced.

E(Ag/AgCl ref electrode) = 0.197 V
$E^0(Fe^{3+}/Fe^{2+})$ = 0.771 V

Draw a sketch of the typical standard curve obtained from such an experiment. Label the axis appropriately.

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ $\quad E^0_+ = 0.771$

$E = E_+ - E_- = E^0_+ - 59.16/1 \log([Fe^{2+}]/[Fe^{3+}]) - E_-$

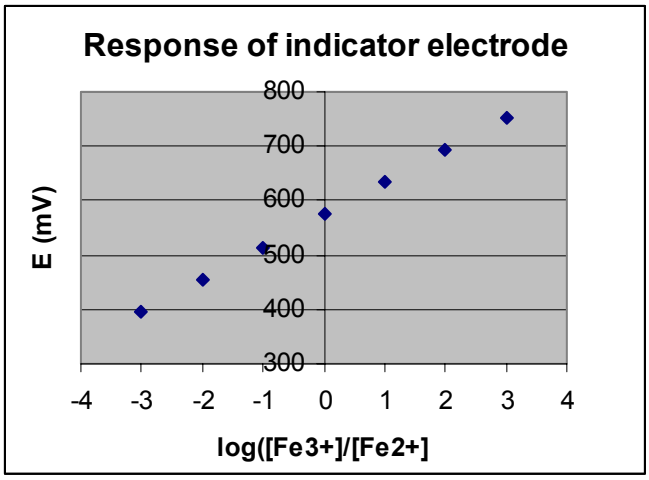
$E = 0.771 - 59.16 \log([Fe^{2+}]/[Fe^{3+}]) - 0.197$

$E \text{ (in mV)} = 574 + 59.16 \log ([Fe^{3+}]/[Fe^{2+}])$

The cell voltage changes by about 59 mV for every factor of 10 change in the $[Fe^{3+}]/[Fe^{2+}]$ ratio.

Ratio	log (ratio)	E
0.00100	-3	397
0.0100	-2	456
0.100	-1	515
1.000	0	574
10.00	1	633
100.0	2	692
1000	3	751

Plot E vs, log (ratio)



Why does the junction potential at the salt bridge limit the accuracy of a single measurement and why does the application of a standard curve address this issue?

As long as the ionic strength of the unknown is similar to that of the standards, the junction potential is constant. By plotting the data the junction potential is accounted for as part of the intercept, and does not produce an inaccurate result.