

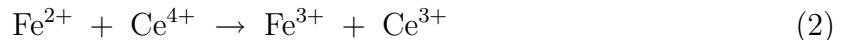
Potentiometric titration

Consider an electrochemical cell



where half-cell 2 may consist of, say, $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the other half-cell is a reference electrode.

If we titrate the content in half-cell 2 with another redox system, say with Ce^{4+} -ions, which then become reduced to Ce^{3+} -ions, the reaction



takes place, and for this system the process occurs rapidly. If we initially have n_o mmol of Fe^{2+} , then after addition of n mmol of Ce^{4+} , we have (almost) $n_o - n$ mmol Fe^{2+} , n mmol of Fe^{3+} and Ce^{3+} and a vanishingly small concentration of Ce^{4+} in half-cell 2.

The EMK of the cell is thus conveniently calculated from the reasonably well defined concentrations of the iron system, and we find

$$E = E_{Fe} - \frac{N}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad (3)$$

$$= E_{Fe} - \frac{N}{1} \log \frac{n_o - n}{n} \quad (4)$$

This will yield a value of E in the neighborhood of E_{Fe} .

However, when the titration is complete (when $n = n_o$), Fe^{2+} is (almost) removed. Further titration yields a surplus of Ce^{4+} in half-cell 2 of $n - n_o$ mmol, and a constant value of n_o mmol of Fe^{3+} and Ce^{3+} . In this case it is most easy to calculate E from the redox potential of the Ce system:

$$E = E_{Ce} - \frac{N}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \quad (5)$$

$$= E_{Ce} - \frac{N}{1} \log \frac{n_o}{n - n_o} \quad (6)$$

Now we obtain a value of E close to E_{Ce} . The two redox potentials are 0.771 V and 1.61 V, respectively. We thus observe a jump in E from approx. 0.771 V to 1.61 V for half-cell 2, when we pass the equivalence point $n = n_o$.

Since this jump may conveniently be observed, it is possible to read out added Ce^{4+} (that is n) at this point, from which we then determine the original amount n_o of Fe^{2+} .