# Potentiometric titration

Consider an electrochemical cell

$$\text{reference}||\text{ox}_2, \text{red}_2|\text{Pt} \tag{1}$$

where half-cell 2 may consist of, say, $Fe^{2+}/Fe^{3+}$ 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

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+} \tag{2}$$

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

$$E = E_{Fe} - \frac{N}{1} log \frac{[Fe^{2+}]}{[Fe^{3+}]} \tag{3}$$

$$= E_{Fe} - \frac{N}{1} log \frac{n_o - n}{n} \tag{4}$$

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:

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

$$= E_{Ce} - \frac{N}{1} log \frac{n_o}{n - n_o} \tag{6}$$

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 $Fe^{2+}$.