

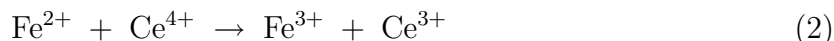
# Potentiometric titration

Consider an electrochemical cell

$$\text{reference} || \text{ox}_2, \text{red}_2 | \text{Pt} \quad (1)$$

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  $\text{Ce}^{4+}$ -ions, which then become reduced to  $\text{Ce}^{3+}$ -ions, the reaction



takes place, and for this system the process occurs rapidly. If we initially have  $n_o$  mmol of  $\text{Fe}^{2+}$ , then after addition of  $n$  mmol of  $\text{Ce}^{4+}$ , we have (almost)  $n_o - n$  mmol  $\text{Fe}^{2+}$ ,  $n$  mmol of  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$  and a vanishingly small concentration of  $\text{Ce}^{4+}$  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  $n = n_o$ ),  $\text{Fe}^{2+}$  is (almost) removed. Further titration yields a surplus of  $\text{Ce}^{4+}$  in half-cell 2 of  $n - n_o$  mmol, and a constant value of  $n_o$  mmol of  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$ . 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  $\text{Ce}^{4+}$  (that is  $n$ ) at this point, from which we then determine the original amount  $n_o$  of  $\text{Fe}^{2+}$ .