

Applying the Nernst equation (which is given on the data sheet) to the  $(M^{2+}|M)$  couple then gives:

$$\begin{aligned} E &= E^\ominus - (RT/2F) \ln \{a(M)/a(M^{2+})\} \\ &= E^\ominus + (RT/2F) \ln a(M^{2+}), \text{ since } a(M) = 1 \\ &= [-0.40 + (-0.42)] \text{ V} = -0.82 \text{ V} \end{aligned}$$

[Comment See Block 7, Section 6.2.3 and SAQ 24 for similar examples.]

(b) The metal M will have a tendency to corrode (under the specified conditions) if  $E = E_{ca} - E_{an} > 0$ , where

(i)  $E_{an} = E(M^{2+}|M)$  with  $a(M^{2+}) = c(M^{2+})/c^\ominus = 10^{-6}$  (the criterion for corrosion established in Topic Study 3, Section 2).

So

$$\begin{aligned} E_{an} &= E^\ominus(M^{2+}|M) + (RT/2F) \ln 10^{-6} \\ &= [-0.40 + (-0.177)] \text{ V} = -0.58 \text{ V} \end{aligned}$$

(ii)  $E_{ca}$  is the electrode potential of the appropriate cathodic reaction. In general, this can be either:



or



From these values, oxygen reduction will always provide the more positive value of  $E_{ca}$ , and in aerated water it is also the more likely process. Applying the Nernst equation:

$$E = E^\ominus - (RT/2F) \ln \frac{a(H_2O)}{\{a(O_2)\}^{1/2} \{a(H^+)\}^2}$$

Assuming  $a(H_2O) = 1$  and  $a(O_2) = p(O_2)/p^\ominus = 1$  (that is,  $p(O_2) = 1$  bar), and given the definition of  $pH = -\log a(H^+)$ , this reduces to:

$$\begin{aligned} E &= E^\ominus - 0.0592 \text{ pH} \\ &= 0.93 \text{ V at pH 5} \end{aligned}$$

Thus,  $E = E_{ca} - E_{an} > 0$ , and the metal does have a tendency to corrode.

A further assumption is that at pH 5, the metal is unlikely to be pushed into the passivation domain by formation of a surface film of insoluble hydroxide.

(c) There are several possible experiments that could be described here. The two that are discussed in some detail in Topic Study 3 are the drop experiment (using an acid/base indicator, together with one for  $M^{2+}$  if possible; cf. iron corrosion) and a cell set up with metal M electrodes in which oxygen is passed over one of these. [You should describe only *one* of these experiments.]

This type of corrosion occurs when a metal in contact with a solution is exposed to different oxygen concentrations. Typical examples include:

- when a paint surface is chipped;
- existence of crevices in a metal surface;
- metal pipes above and below water lines;
- metal pipes embedded in sand and below water;
- metal pipes passing through soils of different oxygen permeability.