Chemistry 201

The pH dependence
of electrochemical potential

NC State University

Using the Nernst equation

We can use the Nernst equation to calculate the Half cell potential at pH 7.

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^o = +0.0\ V$$

eqn. $\mathrm{E = E^0 - \frac{RT}{nF} \ln Q}$ with $\mathrm{E^0 = 0.0\ V}$ gives

$$\mathrm{E = \frac{RT}{nF} \ln \frac{[H^+]^2}{P_{H_2}}}$$

where we have used the stoichiometry of the half cell reaction. The constants are can be evaluated to be:

$$\mathrm{\frac{RT}{F} = \frac{\left(8.31 \frac{J}{mol\ K}\right)(298\ K)}{96{,}472} = 0.0256\ V}$$

Calculating the cell potential at pH = 7

Therefore, the cell potential of hydrogen electrode is

$$E = \frac{RT}{nF} \ln \frac{[H^+]^2}{P_{H_2}}$$

Now, we put in the conditions of a pH = 7 electrode,

$$E = \frac{0.0256}{2} \ln [H^+]^2 \ V$$

which can be evaluated to give

$$E = 0.0256 \ \ln(10^{-7}) \ V = -0.413 \ V$$

Calculating the pH dependence of E

For each factor ten change in $[H^+]$, that is to say, for each decrease in pH unit, the cell potential changes by:

$$E = 0.0256 \ln(10^{-1})\ V = -0.059\ V$$

This means that we can write the SHE as:

$$E = 0.059pH - 0.0128 \ln P_{H_2}\ V$$

Thus, we can correct for H_2 partial pressure as well.