

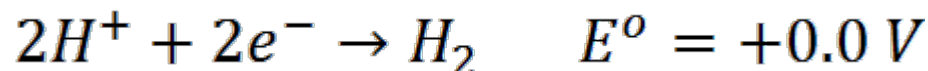
# Chemistry 201

## The pH dependence of electrochemical potential

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# Using the Nernst equation

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



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

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

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

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

# 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,

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

which can be evaluated to give

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

# 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:

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

This means that we can write the SHE as:

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

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