

Electrochemistry Primer

1 Half reactions

Consider one half-reaction $\sum_n \nu_n^L X_n^L \rightarrow \sum_m \nu_m^R X_m^R$ so that ν_1^L moles of a species X_1^L , ν_2^L moles of species X_2^L , ... and so on react to form ν_1^R moles of a species X_1^R , ν_2^R moles of species X_2^R , ... and so on.

If z electrons appear on the right-hand-side of the reaction, then all of the following are true:

- electrons are *withdrawn* from the reactants
- we say the reactants are *oxidized*
- we say the reactants are *reducing* agents
- we say the reaction is an *oxidation* reaction

Likewise, if the electrons appear on the left-hand-side of the equation:

- the reactants *gain* electrons from the reaction
- we say the reactants are *reduced*
- we say the reactants are *oxidizing* agents
- we say the reaction is a *reduction* reaction

Now suppose we place an initially uncharged sensing electrode in a solution containing some mixture of the reactants of products of some redox half-reaction. Suppose for the sake of concreteness that z electrons appear on the right-hand-side of the equation of this half-reaction so that we are formally considering an oxidation reaction. Let ΔG^o represent the change in the Gibbs free energy associated with this half-reaction. In other words, we assume that:

- if z electrons are transferred by the half-reaction from solution to the initially uncharged sensing electrode, then
- the change in the Gibbs free energy of the solution is $\frac{\Delta G^o}{N_A}$

where N_A is Avogadro's number. We assume that the capacitance C between the electrode and the solution is large enough that we can ignore the electrical energy

$\frac{1}{2} \frac{Q^2}{C}$ associated with the charge transfer charge transfer $Q = z \times e$ between the electrode and solution¹.

Once the initially uncharged sensing electrode is placed in the solution, one of two things can happen:

- If $\Delta G^o < 0$, then the oxidation reaction will proceed spontaneously, and a non-negligible number of electrons will start to accumulate on the sensing electrode. After x moles of electrons are transferred to the electrode, there will be a charge $Q = -xF$ on the sensing electrode, where F is the Faraday constant. This in turn implies that there will be an electric potential difference $\Phi = \phi_s - \phi_l = \frac{Q}{C} = -\frac{xF}{C}$ between the (s)olid electrode and the (l)iquid solution, where C is again the electrical capacitance between the electrode and the solution.

Now for every z electrons transferred to the sensing electrode by the oxidation reaction, the change in the Gibbs free energy is now no longer simply $\frac{\Delta G^o}{N_A}$ because we must also take into account the electrical energy $\frac{\Delta G_e}{N_a} = q\Phi = -ze\Phi = \frac{zexF}{C}$ required to transfer z electrons from the solution to the electrode. Note that this energy ΔG_e is necessarily *positive* and so that the overall driving force $\Delta G = \Delta G^o + \Delta G_e$ of the oxidation reaction increases towards zero from ΔG^o as the oxidation reaction proceeds.

When enough electrons have accumulated on the sensing electrode that $\Delta G = 0$, then there is no more driving force for the reaction and equilibrium is achieved. From some simple algebra we find that this occurs when

$$\Phi = \frac{\Delta G^o}{zF} \quad (1)$$

Note that this equation implies that the equilibrium electrical potential $\Phi = \phi_s - \phi_l$ between the electrode and the solution is *negative*, which is consistent with our picture of negatively charged electrons accumulating on the (s)olid electrode and positive ions accumulating in the (l)iquid solution.

Incidentally, how many moles x of reactants do we need to consume before equilibrium is reached? From the earlier expression $\Phi = -\frac{xF}{C}$ we find that, for a reasonable capacitance of $C \approx 1$ nF and $\frac{\Delta G^o}{N_A} \approx 1$ eV (also reasonable), this occurs after only $x \approx 10^{-14}$ moles of electrons are transferred to the sensing electrode. This corresponds for all practical purposes to a completely negligible change in the concentrations of reactants and products, so that, for instance, we do not need to consider any possible change in the standard Gibbs potential ΔG^o as the sensing electrode charges.

¹In order for the electrical energy to be negligible, we need $\frac{|\Delta G^o|}{N_A} \gg \frac{1}{2} \frac{(ze)^2}{C}$. Taking $z = 1$ and assuming a reasonable $\frac{|\Delta G^o|}{N_A}$ of 1 eV, we find that the electrical energy is negligible so long as $C \gg \frac{1}{2} \frac{e^2}{V} \approx 10^{-19}$ F, which is a microscopically small capacitance, so that this condition is easily met. A spherical capacitor with a capacitance this small would for instance have a radius of just 1 nm.

- If $\Delta G^o > 0$, then the opposite (*reduction*) reaction will proceed spontaneously. Now the sensing electrode will gradually *lose* electrons, so that a *positive* electric charge will build up on the sensing electrode. The resulting potential Φ will now be *positive* but the direction of charge transfer is reversed from the oxidation ($\Delta G^o < 0$) case, so that there is still a *positive* ΔG_e opposing the *negative* $-\Delta G^o$ driving force of the reduction reaction. Following the same steps, we arrive at the same result:

$$\Phi = \frac{\Delta G^o}{zF}$$

As an exercise, redo the above analysis for a half-reaction where the z electrons instead appear on the left-hand-side of the reaction so that we are formally considering a *reduction* reaction. Show that the expression for Φ changes by a negative sign. Is this what you expect?

2 Full reaction

Now suppose we make an ionically conductive connection (using, e.g., a salt bridge) between the two half-cells A and B so that $\phi_i^A = \phi_i^B$. If we take a voltmeter and connect its positive terminal to sensing electrode B and its negative terminal to sensing electrode A , then when each half-cell is individually at equilibrium the voltmeter will read:

$$\begin{aligned} E_{BA} &= \phi_s^B - \phi_s^A \\ &= (\phi_s^B - \phi_l^B) - (\phi_s^A - \phi_l^A) \\ (!) &= \frac{1}{F} \left(\frac{\Delta G_B^o}{z_B} - \frac{\Delta G_A^o}{z_A} \right) \end{aligned} \tag{2}$$

Note: in the step marked (!) we apply equation (1), which was derived under the assumption that ΔG^o is the standard change in Gibbs energy for the *oxidation* reaction. If ΔG^o is instead understood to refer to the change in Gibbs energy for the reverse (*reduction*) reaction, we must make the substitution $\Delta G^o \rightarrow -\Delta G^o$.

E_{BA} is known as the *redox potential* of the full-cell reaction. Suppose now that we replace the voltmeter, which has a very high electrical resistance, with an electronically conductive connection (e.g. with metallic wire) between the two sensing electrodes. If E_{BA} was initially positive, then electrons will instantly conduct from electrode A to electrode B until the potential between the electrodes is zero.

This charge transfer throws the two half-reactions out of equilibrium. The removal of the negatively-charged electrons from electrode A will reduce the barrier to the oxidation reaction in half-cell A , while the addition of electrons to electrode B will reduce the barrier to the reduction reaction.

If the oxidation reaction in A is initially more rapid than the reduction reaction in B , then the electrodes (which are at the same potential) will become

gradually more negatively charged and the solutions (which are at the same potential) will become gradually more positively charged. The resulting change in the potential difference between the electrodes and the solutions will act to slow the oxidation reaction in A and speed up the reduction reaction in B until eventually the reaction rates in the two half-cells become equal. A new dynamic equilibrium is thus achieved, with oxidation in A balanced by reduction in B . The reaction of course will not run forever. How is thermodynamic (i.e. static) equilibrium achieved?

Redo the above analysis and work out what happens when:

- $E_{BA} > 0$ as before, but now the reduction reaction in B is initially more rapid than the oxidation reaction in A .
- $E_{BA} < 0$. In which half-cell does the oxidation reaction now occur?

3 Redox reactions

Now suppose the solutions of the two half-cells are mixed together and the electrodes are removed. What will happen? We no longer have a metal electrode to serve as a reservoir for the addition and removal of electrons, so the half-reactions can not individually occur. However, if the oxidation half-reaction B produces $z_A \times z_B$ electrons, then oxidation half-reaction A can run *in reverse* and consume those $z_A \times z_B$ electrons. This is known as a *redox reaction*. Maintaining the convention that ΔG^o is the standard change in Gibbs associated with the *oxidation* half-reaction, then the total change in the Gibbs free energy associated with this process is

$$\begin{aligned} & z_A \times \left(+\frac{\Delta G_B^o}{N_A} \right) + z_B \times \left(-\frac{\Delta G_A^o}{N_A} \right) \\ &= e z_A z_B \times \frac{1}{F} \left(\frac{\Delta G_B^o}{z_B} - \frac{\Delta G_A^o}{z_A} \right) \\ &= e z_A z_B E_{BA} \end{aligned} \tag{3}$$

Where in the last step we used equation (2). Note that with the solutions mixed and the electrodes removed we no longer have macroscopic separation of positive and negative charges. We can therefore neglect the electrical contribution ΔG_e to the Gibbs energy.

Equation (3) tells us that from the redox potential E_{BA} is directly proportional to the ΔG of the associated redox reaction. Further, the two quantities have the same sign, so that by knowing the sign of the redox potential E_{BA} we can predict the spontaneity of the associated redox reaction.

For instance, if $E_{BA} < 0$, then the oxidation half-reaction B and reverse (reduction) half-reaction A proceed spontaneously. In other words, electrons are spontaneously transferred from B to A so that we can say A oxidizes B (or, equivalently, that B reduces A). If $E_{BA} > 0$ we obtain of course the opposite conclusion. Indeed you can verify for yourself that the direction in which a redox

reaction proceeds is the same as the direction of the associated full-cell reaction when the two sensing electrodes are shorted together with a metal wire. The energetics of the two reactions (redox reaction vs. full-cell reaction) are in fact the same and differ only in the reaction mechanism. When the solutions are mixed in the absence of electrodes, the electrons are directly transferred from the reducing agent being oxidized to the oxidizing agent being reduced, while in the full-cell reaction the electrons produced in the oxidation half-cell first travel across the wire before reducing the oxidizing agents in the reduction half-cell.

Note that the conclusions of the previous paragraph are *independent* of our convention to associate ΔG^o with the oxidation reaction. The adoption of this convention only helped us to arrive at the conclusions. The only convention required is that a redox potential E_{BA} refer to the electric potential difference $\phi_s^B - \phi_s^A$ (and *not* $\phi_s^A - \phi_s^B$).

4 Standard electrode potential

The *standard electrode potential* $E^o(B)$ associated with a half-cell B is simply the potential E_{BA} when half-cell A is the standard hydrogen electrode. If we know $E^o(B)$ and $E^o(C)$ for half-reactions B and C , then we can solve for the redox potential E_{CB} :

$$\begin{aligned} E_{CB} &= \frac{1}{F} \left(\frac{\Delta G_C}{z_C} - \frac{\Delta G_B}{z_B} \right) \\ &= \frac{1}{F} \left(\left(\frac{\Delta G_C}{z_C} - \frac{\Delta G_A}{z_A} \right) - \left(\frac{\Delta G_B}{z_B} - \frac{\Delta G_A}{z_A} \right) \right) \\ &= E_{CA} - E_{BA} \\ &= E^o(C) - E^o(B) \end{aligned} \tag{4}$$

5 Application

In our problem, we are given the standard electrode potentials for half-reactions $A^+ + e^- \rightarrow A$, $B^+ + e^- \rightarrow B$. Let's consider for concreteness the case where $E^o(A) = -1.0\text{ V}$ and $E^o(B) = -1.1\text{ V}$. To determine whether A oxidizes B or vice-versa, we inspect their redox potential

$$E_{BA} = E^o(B) - E^o(A) = (-1.1\text{ V}) - (-1.0\text{ V}) = -0.1\text{ V} < 0$$

Using the rule derived in the previous section we can conclude that B will reduce A , or that in other words A will oxidize B .