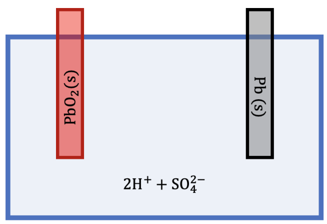
# Lead-Acid Batteries

Douglas H. Laurence

Department of Physical Sciences, Broward College, Davie, FL 33314

A very common type of battery is a lead-acid battery, which uses conductive lead terminals placed in an acid bath to produce a separation of charges between the terminals, and thus a voltage. A common example is a car battery, which is a 12V lead-acid battery composed of one lead (Pb) terminal, one lead(IV) oxide ($PbO_2$) terminal, and a sulfuric acid ($H_2SO_4$) bath. Let's call the lead terminal the "black terminal" and the lead(IV) oxide terminal the "red terminal." The general structure of this type of battery is shown in the figure below.




At the red terminal, the reaction is given by:

$$PbO_2(s) + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$

At the red terminal, solid lead(IV) oxide ($PbO_2$) is converted into solid lead(II) sulfate ($PbSO_4$). Electrons are required to run this reaction, leaving the terminal positive overall. Thus, the terminal composed of lead(IV) oxide is the positive terminal; knowing this in advance, I chose it to be the red terminal.

At the black terminal, the reaction is given by:

$$Pb(s) + HSO_4^- \rightarrow PbSO_4(s) + H^+ + 2e^-$$

At the black terminal, solid lead (Pb) is converted into solid lead(II) sulfate ($PbSO_4$), producing electrons each reaction. This leaves the black terminal negative overall. Thus, the terminal composed of lead is the negative terminal; knowing this in advance, I chose it to be the black terminal.

Notice something about the reaction at each terminal: every reaction at the positive terminal converts one $PbO_2$ into one $PbSO_4$, and every reaction at the negative terminal converts one Pb into one $PbSO_4$. So, assuming that the positive terminal began with roughly as much $PbO_2$ as Pb on the negative terminal, the reaction will end when all $PbO_2$ is converted into $PbSO_4$ at the positive terminal, which occurs at the same time as when all Pb is converted into $PbSO_4$ at the negative terminal. So, the final state of the battery is with both terminals being composed entirely of $PbSO_4$, resulting in a dead battery.

Lastly, there's a reaction occurring in the acid solution itself. Sulfuric acid, a strong acid, completely dissociates in water. $HSO_4^-$ must be formed out of hydrogen $H^+$ and sulfate $SO_4^{2-}$.

Note that we need two $HSO_4^-$: one for the positive temrinal and one for the negative terminal. So we'll write the reaction in the solution as:

$$2\mathrm{H}^+ + 2\mathrm{SO}_4^{2-} \;\rightarrow\; 2\mathrm{HSO}_4^-$$

Next, we can calculate the total energy is released adding the energies produced at the positive terminal, negative terminal, and in the solution. The energy we want to know is the Gibbs free energy $G$, which tells us the amount of energy released which can be converted into electrical energy. Finding the change in free energy is simple: $\Delta G = G_f - G_i$.

From standard tables, the relevant Gibbs free energy (of formation) values are:

$$\begin{array}{ll} G_{\mathrm{Pb}} = 0 & G_{\mathrm{H_2O}} = -237{:}13\ \mathrm{kJ/mol} \\ G_{\mathrm{PbO_2}} = -217{:}33\ \mathrm{kJ/mol} & G_{\mathrm{PbSO_4}} = -813{:}0\ \mathrm{kJ/mol} \\ G_{\mathrm{HSO_4^-}} = -755{:}91\ \mathrm{kJ/mol} & G_{\mathrm{SO_4^{2-}}} = -744{:}53\ \mathrm{kJ/mol} \\ G_{\mathrm{H^+}} = 0 & \end{array}$$

At the positive terminal, the reaction yields the following change in Gibbs free energy:

$$\begin{aligned} \Delta G_+ &= G_{\mathrm{PbSO_4}} + 2G_{\mathrm{H_2O}} - G_{\mathrm{PbO_2}} - G_{\mathrm{HSO_4^-}} - 3G_{\mathrm{H^+}} \\ &= (-813{:}0) + 2(-237{:}13) - (-217{:}33) - (-755{:}91) \\ &= -314{:}02\ \mathrm{kJ/mol} \end{aligned}$$

At the negative terminal, the reaction yields the following change in Gibbs free energy:

$$\Delta G_- = G_{\mathrm{PbSO_4}} + G_{\mathrm{H^+}} - G_{\mathrm{Pb}} - G_{\mathrm{HSO_4^-}} = (-813{:}0) - (-755{:}91) = -57{:}09\ \mathrm{kJ/mol}$$

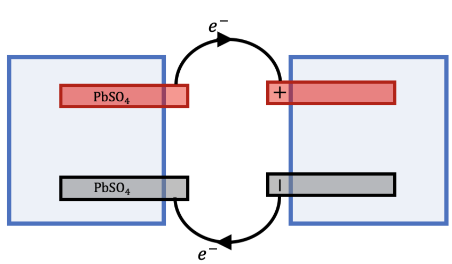
And, lastly, the reaction in the solution yields the following change in Gibbs free energy:

$$\Delta G_{\mathrm{soln}} = 2G_{\mathrm{HSO_4^-}} - 2G_{\mathrm{H^+}} - 2G_{\mathrm{SO_4^{2-}}} = 2(-755{:}91) - 2(-744{:}53) = -22{:}76\ \mathrm{kJ/mol}$$

Adding up all the Gibbs free energy changes, the complete reaction has a change of:

$$\Delta G_{\mathrm{rxn}} = \Delta G_+ + \Delta G_- + \Delta G_{\mathrm{soln}} = (-314{:}02) + (-57{:}09) + (-22{:}76) = -393{:}87\ \mathrm{kJ/mol}$$

Note that the change in Gibbs free energy for the entire reaction is negative, meaning that energy is *released* by this reaction, as we would expect (this is the energy required to power the battery). In fact, energy is released for each of the three individual reactions in these batteries; this is important, because a reaction won't be spontaneous unless $\Delta G$ is negative for the reaction.




Consider the process of re-charging the battery. To do so, we connect the red terminal of the dead battery to the positive terminal of a power supply, and the black terminal of the dead battery to the negative terminal of the power supply, as shown in the above figure. The negative terminal of the power supply drives electrons into the black terminal of the dead battery with enough energy to reverse the reaction at the black terminal:

$$PbSO_4(s) + H^+ + 2e^- \rightarrow Pb(s) + HSO_4^-$$

The $\Delta G$ for this reaction would be positive, and thus requires energy; this energy is provided by the power supply recharging the battery. Likewise, the positive terminal of the power supply pulls electrons from the red terminal of the dead battery, forcing the reaction at the red terminal to reverse itself:

$$PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + HSO_4^- + 3H^+ + 2e^-$$

As with the reverse reaction at the black terminal, this reaction has a positive $\Delta G$, and so requires energy to be input; this energy comes from the power supply recharging the battery.

Now that we know how much electrical energy is produced per reaction, we can compute the voltage of the battery. Recall that potential difference $\Delta$ – another name for voltage $V$ – is just the change in energy divided by the charge:

$$\Delta \quad = \frac{\Delta E_{\text{rel}}}{Q}$$

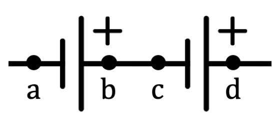
where $\Delta E_{\text{rel}}$ is the energy released per reaction and $Q$ is the total charge released per reaction. Note that 2 electrons are released in the reaction, there are $6{:}02 \times 10^{23}$ electrons per mol (the definition of a mol), and each electron has a charge of $1{:}6 \times 10^{-19}$ C. So, the charge $Q$ released per reaction is:

$$Q = 2 * 6{:}02 \times 10^{23} \ \frac{\text{electrons}}{\text{mol}} * 1{:}6 \times 10^{-19} \ \frac{\text{C}}{\text{electron}} = 192{;}640 \ \frac{\text{C}}{\text{mol}}$$

Plugging this result into the above equation for voltage, we find:

$$V = \frac{393{;}870 \text{ J/mol}}{192{;}640 \text{ C/mol}} = 2{:}04\text{V}$$

Notice that a single unit – one box shown in the figure on the first page – only produces 2V, when 12V are required to power a car. We call these single units ”cells” of the battery, and a complete 12V battery requires 6 cells. To see why this is true, it’s important to understand how batteries act when connected in series.




Imagine two batteries connected in series, as shown in the above figure. If you connect batteries in series, with their polarities aligned, then the total voltage is just the sum of each individual cell voltage. For example, in the above figure, the total voltage from $a$ to $d$ is:

$$\Delta \ _{ad} = \Delta \ _{ab} + \Delta \ _{bc} + \Delta \ _{cd}$$

Note that the ideal wire is assumed to have negligible voltage, so $\Delta \ _{bc} = 0$. If the first battery has a voltage of $V_1$, that means that the positive terminal (at point $b$) is $V_1$ volts higher than the negative terminal (at point $a$), so:

$$\Delta \ _{ab} = \ _b - \ _a = V_1$$