

Salt bridges

Both your textbook and the laboratory manual bandy about the term salt bridge so nonchalantly that it seems as if everyone should automatically know what they are. While it is true that most students have a basic understanding of what purpose a salt bridge serves, experience shows that they often totally misunderstand how a salt bridge works. Here, we address the concepts in a straightforward (we hope) question and answer format.

What purpose does a salt bridge serve?

In an electrochemical cell, the salt bridge maintains electroneutrality and allows a current to flow. Otherwise, there would be a pile-up of electrons, and the current would stop. *Galvanic* cells absolutely require salt bridges or some other means to close the circuit and allow current to flow. Galvanic (also called *voltaic*) cells are powered by chemical reactions that are spontaneous under the experimental conditions. This means that the reactions go by themselves; it does not mean they are fast. Remember that two different ways to say a reaction is spontaneous are $E > 0$ and $\Delta G < 0$.

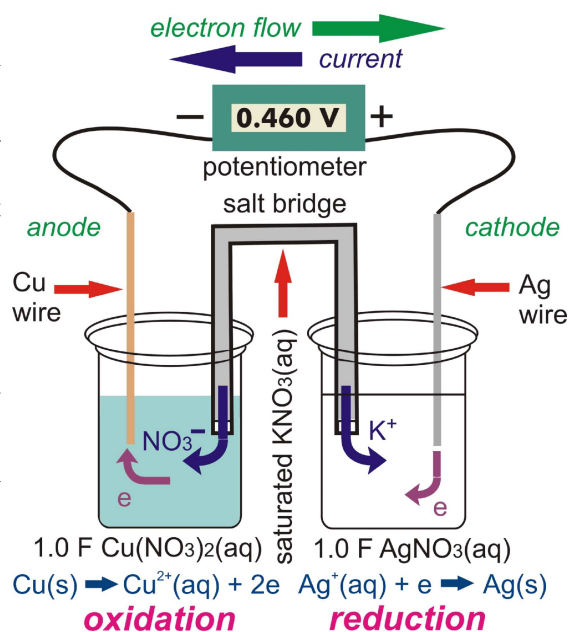
Why is a salt bridge necessary? Why not just mix the reactants together?

The purpose of an electric circuit is to obtain electrical work from a chemical system at a nearly constant rate. If there were no salt bridge, the reactants would simply mix together and react directly rather than sending electrons through a wire. Their attitude is “Why do electric work if you don’t have to?” Consequently, no current would flow, and there would not be a cell.

Electrolytic cells do not require salt bridges. Since the reaction is not spontaneous and does not take place until you apply an electric potential, no reaction occurs even when all the reagents are mixed together. The various species are already at equilibrium. You disrupt the equilibrium when you apply the potential that causes a current to flow. It is possible to put a salt bridge in an electrolytic cell, but there is no requirement to use one. Most of the time, a salt bridge would be a nuisance.

How does the salt bridge allow current to flow?

Ions do not flow through a salt bridge. The ions flow out of it. The cations flow out at the cathode, and the anions flow out at the anode. The current produced by the salt bridge is the sum of the flow of the cations and the flow of the anions. See the figure at the right.



When the electric current flows through the wire, electrons are transported through the wire from one half-cell (oxidation side, anode) to the other half-cell (reduction side, cathode). This leaves a deficiency of negative charge (surplus of positive charge) on the anode side and produces a surplus of negative charge on the cathode side.

As the figure shows, the cell is gaining cupric cation at the anode (left side), so it needs nitrate anion from the salt bridge to keep the solution electrically neutral. Likewise, the cell is losing silver(I) cation (i.e., gaining Ag^0) at the cathode (right side), so it needs potassium cation to keep the solution electrically neutral. Note that this is a galvanic cell because its reaction is spontaneous.

Does salt flow even when there is no current?

Yes, ions move even when there is no current, but not the same way they move when the cell is running. Ions migrate even when the circuit is broken (e.g., a wire is detached). Why? The salt bridge contains a much higher concentration of the salt than in either half-cell. Simple diffusion causes a solute to flow from regions of high to low concentration. However, electroneutrality causes them to *flow the same way*. In other words, both the cation and the anion flow out of both sides. More solid salt dissolves so that the concentration remains constant. There is an important difference between how ions flow out when the circuit is closed versus open.

Remember that when the circuit is closed and the galvanic cell is operational, the cations flow out of the salt bridge at the cathode, and the anions flow out at the anode due to the electric field created by the cell potential. On the other hand, salt is simply escaping when the circuit is open. This is called Fickian diffusion. It happens even when the current is flowing. Ficke’s law of diffusion states that, whenever there is a concentration gradient between two geographical regions in any mixture of solutions, the particles will move around to uniformly distribute themselves overall. Remember that a solution is homogeneous by definition, so Fickian diffusion does not occur in a true solution. The half-cell–salt bridge–half-cell system is not homogeneous. Another important point is that the relative rates the ions move are very different when current is flowing versus when Fickian diffusion is occurring by itself. Fickian diffusion is much slower.

Table 1. Summary of motion of ions out of the salt bridge

<i>What flows out of the salt bridge when?</i>	Anode (oxidation) half-cell	Cathode (reduction) half-cell
Galvanic cell is operational; circuit is closed; current is flowing	large amounts Cl^- flows out of salt bridge as part of electric current; small amounts of K^+ and Cl^- flow out of salt bridge due to Fickian diffusion	large amounts of K^+ flows out of salt bridge as part of electric current; small amounts of K^+ and Cl^- flow out of salt bridge due to Fickian diffusion
Galvanic cell is inoperative; circuit is open; current is not flowing	small amounts of K^+ and Cl^- flow out of salt bridge due to Fickian diffusion	small amounts of K^+ and Cl^- flow out of salt bridge due to Fickian diffusion

If we waited long enough, would the solution phases eventually mix?

Yes, Fickian diffusion would eventually bring about a homogeneous solution. In other words, when we said above that *ions do not flow through a salt bridge*, we meant that they do not flow through it during the course of a normal laboratory experiment. Remember that one of the reasons we need the salt bridge is to keep the soluble components of the two half-cells separated. If we waited for all the dissolved solutes to completely homogenize themselves, we would be faced with the problem of reactions occurring directly on the metal wire surfaces. Thus, there would be no electrical work.

One thing to keep in mind is that the typical cell reaction takes place fast enough that the cell we would build in a laboratory would run down long before diffusion could homogenize the solutes. Nevertheless, a *wet cell* is not normally a good way to store energy because of Fickian diffusion. That is why most of the C or D cells or batteries used in flashlights, etc., are dry cells. Diffusion is not a problem in a dry cell. One exception to the diffusion problem in wet cells is a lead storage battery (PbO₂-PbSO₄-H₂SO₄ car battery); you can read about this battery in section 20.7 of your textbook (Brown, LeMay and Bursten's *Chemistry: the Central Science*, 9th edition).

What keeps the inert salt concentration constant inside the salt bridge?

The salt bridge contains a saturated solution of some inert salt, usually NaClO₄, KCl, or KNO₃. The term inert refers to the reactivity relative to the reaction under study. The salt is chosen specifically to be inert based on the rest of the reagents in the system. The salt bridge also contains the solid salt in a heterogeneous equilibrium with the solution phase. Remember that the activity of the solid salt is unity. The solid is a critical part; otherwise, the activities (concentrations) of the ions in the aqueous phase would change, and the potential would change. Whenever salt is lost from the salt bridge, more dissolves to continually re-establish the equilibrium per equation 1.



Where is the salt bridge in a combination (pH) electrode?

Different electrodes are designed slightly differently, but they all have a porous plug made of fritted (sintered) glass, called a junction. This can serve the same function as a salt bridge. It slows down diffusion, but it allows ions under the force of an electric field (potential) to migrate. The best electrodes actually have a double junction, which means they have two of these porous plugs. A salt bridge is formed by placing glass cylinders one inside the other with a single fritted junction in each glass cylinder. The space between the two glass cylinders is filled with a saturated salt solution.

The reference electrode is permanently “sealed” in one of the cylinders in some combination electrodes, meaning it cannot be refilled it when it runs out of material. Most of these electrodes have a silver/silver chloride reference half-cell and a lifetime of about 18 months if used constantly, then they must be replaced. The most expensive ones use a reference half-cell based on platinum and can last for years if properly treated.

The combination electrode also has a partial half-cell sensitive to hydrogen ion, which is exposed to the test solution via the probe tip (normally a special and very fragile glass ball). Again, the placement of the cylinders varies. In other words, the innermost cylinder does not always contain the reference or the analytical half-cell. Of course, the salt bridge always has to be sandwiched between somehow. Many currently available commercial combination electrodes are made in ingenious ways by clever glassblowing with connections to the outside world for refilling and crafty use of plastic covers, caps, and sleeves to keep solutions where they belong or to allow access as needed. In order to know what part is where and how to take the thing apart without breaking it, you usually need the manual.

Where is the salt bridge in a calomel reference electrode?

Just as in the combination electrode, the calomel electrode has a salt bridge formed by a double junction. It has two cylinders, one inside the other. The inner cylinder is normally the $\text{Hg}|\text{Hg}_2\text{Cl}_2$ half-cell, and the outer chamber (between the two cylinders) is the salt bridge. The inner cylinder has a single fritted junction that connects it to the salt bridge, and the outer cylinder has a single fritted junction that connects it to the solution into which it has been immersed.