

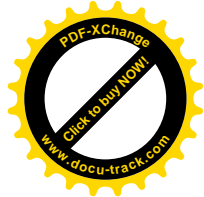
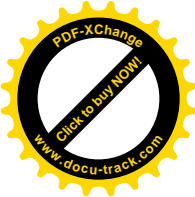
Human Ingenuity Working in Collusion with Molecular Cunning: The World of Galvanic Cells

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I can't but find the Galvanic cells, the devices that produce useful electrical energy from chemical reactions, utterly interesting. To some student of chemistry who somehow, unfortunately, missed the most vital points about the working and formulation of Galvanic cells, they may seem just complicated and somewhat boring, yet of course understandably useful and relevant to his or her life. But one who has understood how cunningly the molecules, atoms, radicals and ions of substances behave within the Galvanic cell to satisfy their rather vested interest of undergoing, as a net result, some thermodynamically spontaneous chemical reaction can only be overwhelmed with a sense of wonder about this whole business. It is equally wonderful to realize the ingenuity of the human Mind, which over the recent centuries has formulated and constructed a wide variety of these devices, compelling the molecules and ions to contribute for human use a share of their chemical energies as they proceed along in their own, selfish reaction-agenda.

As one of the simplest examples, let us first consider the Daniel cell, consisting of a Zn-electrode dipped in a zinc salt solution within one compartment and a Cu-electrode dipped in a cupric salt solution within another, the compartments being separated by a non-reacting salt-bridge. We know that Zn-atoms from the Zn electrode become Zn^{2+} ions in the first compartment, while Cu^{2+} ions become Cu atoms in the second, so that externally electrons flow from the first electrode to the second. To any avid student of chemistry the question that immediately strikes is: why does here Zn becomes Zn^{2+} , and Cu^{2+} becomes Cu? Some people try to explain this from an idea that conversion of Zn to Zn^{2+} is spontaneous as the $\text{Zn}^{2+}|\text{Zn}$ reduction potential is negative (i.e., with standard value -0.76 V), and so on (i.e., positive) for Cu^{2+} to Cu conversion. But this sort of talking is wholly fallacious: Cu^{2+} to Cu reduction per se is not spontaneous (spontaneity-question for a lone electrode-process is simply preposterous, even though that was once asked in a public examination in Assam) but the case is rather that somehow the $\text{Cu}^{2+}|\text{Cu}$ system feels (senses) that on the other compartment there is the $\text{Zn}^{2+}|\text{Zn}$ system, so that the combined (net) redox reaction would be the spontaneous one (i.e., $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ reaction) if and only if the Cu^{2+} ions get converted to Cu (i.e., neither remaining inactive, nor reacting the opposite way). The proof of this other-compartment sensing conjecture is that had $\text{Ag}^+|\text{Ag}$ remained at the other compartment, the behaviour of the $\text{Cu}^{2+}|\text{Cu}$ couple would have been just the opposite. Can you feel the apparently intelligent choice that the Cu^{2+} ions are making?

Of course, had the Zn-atoms are in physical *contact* with the Cu^{2+} ions (as in the case of the familiar high-school experiment of a Zn-rod -- instead of an iron knife -- dipped in a blue vitriol solution), there won't have been much to be astonished about -- it is the natural *wont* of Zn-atoms to react with Cu^{2+} ions, similar to what the Assamese children's rhyme reasons about the cackling of frogs. But Galvanic cells, as this author likes to emphasize, are devices in which the oxidation and the reduction reaction-processes (of the overall reaction) take place at *separate places* (compartments), so that performance of the net

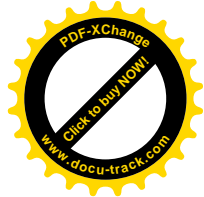
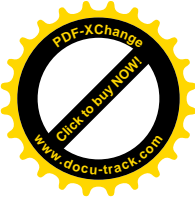


spontaneous redox-reaction ultimately requires transfer of electric current across a distance, which current may then be utilized for human use. [If the Zn-atoms are allowed to meet the Cu^{2+} ions straight at handshaking distance, we won't get any electric current across the wire!]. So the atoms/ ions/ molecules of one chemical species (e.g., Zn-atoms & Zn^{2+} ions) in the Galvanic cell have to make a sort of intelligent choice about the direction of its own reaction, taking consideration of what chemical species (e.g., Cu & Cu^{2+}) are present in the other compartment some distance away. I haven't yet made out how exactly the species in one compartment sense the presence of what's there in the other chamber -- but feel that it must be some electric-potential sensing via the external electronic-conductor (wire) connection, and surely not involving the few stray other-compartment ions that would creep in through the prohibitory salt-bridge. I hope the exact explanation is remaining in some book!

Another wonderful example of such molecular cunning arises in the concentration cells. Let us, as an example, consider a Galvanic cell containing two electrode compartments each with a Cu-electrode dipped in an aqueous CuSO_4 solution, but with different CuSO_4 concentrations in each, these two compartments being connected via a KCl salt-bridge. Here we see that in the lower-concentration compartment Cu-atoms from the electrode steadily dissolves into the blue vitriol solution forming Cu^{2+} ions, while in the higher-concentration compartment Cu^{2+} ions steadily become Cu-atoms, fattening the Cu-electrode there. Why does this happen – is it because of some inherent spontaneity of the Cu- Cu^{2+} inter-conversion reaction? No, surely not, but simply because the Cu^{2+} ions likes to travel from its higher-concentration region to its lower-concentration one. But, as the spoilsport salt-bridge is standing in the way of direct ionic immigration, it takes the awkward route of converting itself into Cu-atoms in the higher-concentration compartment and of getting generated from Cu-atoms in the lower-concentration compartment. So intelligent, isn't it?

The story of human ingenuity about Galvanic cells is, naturally, not as ancient as that of molecular cunning. The earliest inventors and users of Galvanic cells in ancient, before-Christ Mesopotamia and Egypt most probably were totally ignorant about their molecular mechanism. In modern era also, the fresh invention by Galvani in Italy at the eighteenth century was rather accidental. Yet, the human race caught up fast with the mischievous activities of the microscopic particles within the Galvanic cells, and soon became able to design newer such cells better suited with its own cost and convenience considerations.

One of the best examples of highly convenient but yet cost-effective design of man-made Galvanic cells is probably the 'acidic' dry cell, the one that we use everyday in torch-lights, radios and children's toys. They consist of an inner graphite rod, ammonium chloride, manganese dioxide and a covering zinc cylinder. As here the $\text{NH}_4\text{Cl-MnO}_2$ electrolyte paste is separated from the outer zinc cylinder by an inner cardboard cylinder, the reductant (Zn) and the oxidant (MnO_2) can't come in hand-shaking contact, so that the oxidation (i.e., $\text{Zn} \rightarrow \text{Zn}^{2+}$) and the reduction ($2 \text{MnO}_2 + 2 \text{NH}_4^+ \rightarrow \text{Mn}_2\text{O}_3 + 2 \text{NH}_3 + \text{H}_2\text{O}$) processes must happen at *separate* places, requiring a flow of electrons from the zinc rod to the graphite rod to complete the spontaneous *net redox reaction* (this is the electron-flow that we use for producing light, musical sound or toy-movements).



Akin to the well-known quote about the strength of nations, I don't know if anybody ever told -- "show me a spontaneous redox reaction, and I will show you a possible Galvanic cell"! But yet, in many cases, spontaneous redox reactions with even cheap reactants (one of the cheapest example is probably methanol burning in air, this reaction already been translated into a Galvanic cell) have been designed to run in a Galvanic cell, and its reaction-energy harnessed to give us energy in the cleanest and the most convenient form, that is as electric energy. The trick lies in transforming the observed net redox reaction (say, waste paper burning in your backyard) into a combination of an oxidation reaction in which electrons are released, and a reduction reaction in which electrons are accepted -- and then these two half-reactions must be designed to take place at two separate places. This reaction-transformation activity is a mental as well as an experimental exercise -- the mentally hypothesized half-reactions must add up (at least on paper) to give the observed reaction, and also each of the separated half-reactions must be designed to actually undergo in real life, that too in a *non-laughable* rate, within the galvanic cell actually designed.

As an example, let's consider the hydrogen-oxygen combustion reaction -- it's very hard to even visualize it as a combination of an electron-releasing half-reaction and another electron-accepting one. But still, scientists have done this in practice -- and that too, meeting the tougher challenge of each half-reaction being designed to proceed at non-negligible rate: let's consider the two half-reactions in a *molten carbonate fuel cell* (MCFC). Here the oxidation half-reaction is $2\text{H}_2 + 2\text{CO}_3^{2-} \rightarrow 2\text{H}_2\text{O} + 2\text{CO}_2 + 4\text{e}^-$, whereas the reduction half-reaction is $\text{O}_2 + 2\text{CO}_2 + 4\text{e}^- \rightarrow 2\text{CO}_3^{2-}$. When someone thus gives us two half-reactions on a platter, it is indeed very easy to sum them up -- let's do that now! Yes, their net sum is obviously $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, which is nothing but our familiar hydrogen-burning reaction.

This illustration very well exemplifies the fuel cells, which by definition are *continuously operating Galvanic cells that use an external and continuous source of reactants, which comprise a substance commonly known as fuel (e.g., hydrogen, methane, methanol etc.) and a common oxidant such as oxygen gas or simply air*. Fuel cells are naturally the crown of Galvanic cell technology, as the reactants used in fuel cells are very cheap and may also be repeatedly refilled upon consumption. The ability to use fuels as Galvanic-cell reactants instead of as boiler-feed in turbines offers rather indescribable convenience for us! First one of them is the great efficiency of near-total transformation of chemical energy into electrical and also into mechanical energy, compared to the Carnot's efficiency barrier (with even a *theoretical* factor of around 0.5 or even 0.3) for conversion of combustion-generated heat energy into mechanical or into electrical energy. Second is the silent, low-temperature and almost automated type of operation of fuel cells. [Of course, in situations where heat energy is the final aim, as in the case of cooking, it may, forever, remain advisable to burn fuels instead of using fuels in fuel cells.] The only challenge in the fuel cell technology is to design such reactive, catalytic surfaces (at low cost) on which the oxidation and the reduction half-reactions will proceed at a suitably fast rate. When human ingenuity will fully win over this challenge, probably even the cellulose and starch molecules at our waste bins will have to apply their armory of cunning to undergo, in a round-about electron-transferring way, their desired degenerative processes!