

Why the Daniell Cell Works!

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Zinc is a more active metal than copper; zinc reacts with dilute hydrochloric acid while copper does not. When zinc immersed in zinc ions is connected to copper in copper ions via a salt bridge in the Daniell cell, electrons flow externally from the anodic zinc(oxidation) to the copper cathode(reduction). $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$ is the net equation. The free energy change for the spontaneous change is -213 kJ ($E^0 = +1.1 \text{ V}$), the enthalpy change is -217 kJ , and $T\Delta S$ is only -4 kJ . Thus there is a net lowering of energy as zinc dissolves forming $2+$ ions while copper ions form atoms on the copper cathode. Since the entropy change is small because of the same number of atoms and ions of the same charge in the reaction, the energy term involving entropy is not significant in driving this reaction. What can the lowering of energy be attributed to? What atomic properties of zinc or copper can account for the direction of this change? In general can some structural reasons be given for the direction of change in common voltaic cells?

The process of metal atoms dissolving to form $2+$ ions can be thought of as involving the following energy processes: (1) the endothermic separation of the atoms from the solid metal, the heat of atomization or sublimation can be used for this process; (2) the endothermic ionization of the gaseous atom to form the doubly positive ion; (3) the exothermic hydration of water molecules around the ion, represented by the heat of hydration. The sum of these energies, when compared for two metal/metal ion couples, then can provide a basis for an atomic explanation for the drive of chemical change. These values are indicated below in kJ/mole . In addition, standard reduction potentials in volts are given for the metal ion/metal combination for each of the metals listed.

While there is agreement in most sources for atomization (sublimation) and ionization energies and for reduction potentials, there are differences for the single ion hydration energies because of theoretical approximations. For example, the ΔH (hyd.) for the Cu^{2+} ion is given as -2122 , -2065 , -2072 , and -2244 kJ in refs 1, 2, 3, 4, respectively. The reason for this is that single ion hydration energies are *not* experimental values but values derived from standard hydration enthalpies with assumed energy considerations of the metal ion in water (see p 160 of ref 3). However, despite the fact that tables of single ion hydration energies from different sources (see each reference) differ in values for each ion, the order of values for the given metal ions is the same in each reference and would not alter the atomic conclusions made in this article. Thus, the conclusions reached in this article are not proven but, rather, derived as theoretical answers.

metal	$\Delta H(\text{atom})^1$	Ion $E(2+)^1$	$\Delta H(\text{hyd.})^2$	Sum	E^0
Cu	340 kJ	2704 kJ	-2064 kJ	980 kJ	+0.34 V
Pb	197	2168	-1486	879	-0.13
Ni	431	2486	-2034	883	-0.25
Fe	414	2323	-1875	862	-0.44
Zn	130	2641	-2009	762	-0.76
Mg	150	2178	-1888	440	-2.34

The difference in energy sums for Cu vs. Zn is about 218 kJ. ($980 - 762 = 218$), which is about equal to the difference in atomization or sublimation energies. Note that, even though it takes more energy to ionize the copper, the hydration energy is more exothermic for the smaller Cu^{2+} ion by

about the same difference in energies. The energy decrease associated with the Daniell cell reaction is mainly due to the tighter bonding in solid copper than in solid zinc. This difference is consistent with comparisons of densities and atom radii for Cu vs. Zn (9.0 vs. 7.1 g/cm^3 and 1.17 \AA vs. 1.25 \AA).

But what about the iron-copper cell? Here Fe is the anode (like zinc) and the cell potential is 0.78 V . The driving force here would not be tighter bonding in Cu since the atomization energy of Fe is higher (its boiling point is higher by almost $500 \text{ }^\circ\text{C}$). Rather it is the approximate 400-kJ difference in ionization energy that favors the production of Fe^{2+} ions over Cu^{2+} ions, even though the hydration energy favors by 200 kJ the hydration of the smaller Cu^{2+} ion (0.72 \AA vs. 0.76 \AA). The stability of 10 electrons in the 3d orbitals of Cu may account for the requirement of more ionization energy for removing two electrons in Cu than for Fe. Thus in iron-copper cell it is the relative ease of ionization of Fe atoms over copper that causes Fe to be the anode instead of Cu. The net reaction: $\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu(s)}$.

The Ni-Cu cell explanation is similar to that of the Fe-Cu cell with the difference in ionization energy of some 200 kJ , favoring the oxidation of Ni despite the greater sublimation energy and lower hydration energy for Ni. The Pb-Cu explanation would follow the path of the Daniell cell, although sublimation energies are closer and the ionization and hydration of the larger Pb^{2+} ion have much smaller magnitudes than Cu^{2+} . (The densities comparison would not be appropriate for the period 6 element, Pb.) Finally, the Mg-Cu cell has such a great difference in potential arising from all the comparisons, low sublimation energy and low ionization of the large Mg atom, accompanied by the relatively high hydration energy of the small Mg^{2+} ion.

It can be seen from the table of values that the order of Sum values (i.e., sum of sublimation, ionization, and hydration energies) match within a few kJ, the order of electrode potentials. Entropy effects have not been considered in this article.

Chemical thermodynamics with its $\Delta G = \Delta H - T\Delta S$ needs no atomic or molecular explanation for predicting the direction of chemical changes. Since differences in entropy changes for metal/metal ion($2+$) couples are small, it is the enthalpy change differences that allow structural interpretations. Thus, the strength of bonds between atoms in metals, the relative ease of removing electrons from atoms, and the energy lowering of the attraction of water molecules for positive ions in solution all aid beginning students' understanding of why reactions occur. The Daniell cell works by the dissolving of the zinc and the plating on the copper cathode, and with a positive potential difference of 1.1 V . It works in that direction and not the reverse (at standard conditions) because copper atoms are more closely and strongly bonded in the solid metal than zinc atoms. In other cells relative ease in ionization or greater stability of hydration can explain the direction of chemical change. It is thus demonstrated that considerations at the atomic level can be helpful in understanding why chemical reactions occur.

Literature Cited

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