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Observations on Lemon Cells

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In many general chemistry texts (*1*), the electrochemistry chapter is introduced with a picture of a "lemon cell", leads of Zn and Cu piercing a lemon (or sometimes a grapefruit). A voltmeter connected across them shows a potential of about 1 V. (It has been shown how several fruits connected in series can be used to run a calculator [*2*].) The texts then discuss oxidation–reduction, half-cells, and the rest of what we teach freshmen about electrochemistry, and the lemon is never mentioned again.

It would appear to be questionable scientific pedagogy to present something, even something as neat as a lemon cell, without explaining how it works. One risks having a thoughtful student ask for an explanation or, worse, having the student assume that the lemon cell illustrates what follows in the text. Generally, this includes the statement that an electrochemical cell requires separation of the oxidation and reduction half-cells, as illustrated by the Daniell cell (Zn^{2+}/Zn and Cu^{2+}/Cu half-cells connected by a salt bridge), presentation of the electrochemical series (half-cell reduction potentials), and use of the Nernst equation. In the lemon cell, there is only one solution, which contains neither Zn^{2+} nor Cu^{2+}, and the measured potential is not the difference of the Zn^{2+}/Zn and Cu^{2+}/Cu reduction potentials. Here, I present some measurements on the lemon cell (or an equivalent system) and interpret them to explain what is actually going on. These experiments could be easily performed by students in the freshman chemistry laboratory.

Experiments

Of course other fruits and vegetables, or just aqueous solutions, can replace the lemon. The orange juice cell (copper and magnesium leads dipping into orange juice) has been discussed in some detail by Kelter et al. (*3*) and used to run a clock. It has been shown that a 5% solution of citric acid imitates the lemon well (*2*). In fact, any acid will do: one of the "Things a Boy Can Do with Electrochemistry" (*4*) is to put Zn and Cu strips into dilute sulfuric acid and observe a voltage. This last arrangement resembles the "cups" made by Volta circa 1800 (see below). It is also well known that other metals can be substituted for Zn and Cu. This, with the placement of the lemon cell at the beginning of the chapter on electrochemistry, suggests that the emf of such a cell is given by the difference of the reduction potentials of the metals.

Accordingly, our first experiments were measurements of the emf's of cells formed by dipping two different metals from Cu, Pb, Zn, Ni, and Fe into a 0.2510 M citric acid solution (4.10% citric acid by weight). The emf is the open-circuit potential difference, right electrode minus left electrode. The results are shown in Table 1, along with the difference in half-cell reduction potentials, right electrode minus left. The emf's correlate very poorly with the reduction potential difference, suggesting that a lemon cell is not equivalent to two metal–metal ion half-cells. The poor correlation could also be caused by differing solution concentrations of different

metal ions, but a tenfold change in concentration would change the emf by only 0.0510 V.

To find out what the cell reaction in the Zn–Cu lemon cell really is, we performed experiments based on the Nernst equation. By convention, the cell reaction is written so that reduction takes place at the right-hand electrode and oxidation at the left-hand electrode:

$$a O_R + b R_L + \ldots \rightarrow p O_L + q R_R + \ldots$$
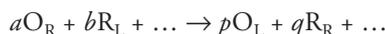
Here, O_R and R_R are the oxidized and reduced species in the right-hand half-cell, R_L and O_L are the reduced and oxidized species on the left, and a, b, p, q, etc. are the stoichiometric coefficients. According to the Nernst equation, the open-circuit potential for this cell is given by

$$E = E_{1/2}^{\circ}(R) - E_{1/2}^{\circ}(L) - \frac{RT}{nF} \ln\left(\frac{[O_L]^p [R_R]^q \ldots}{[O_R]^a [R_L]^b \ldots} \right)$$

where $E_{1/2}^{\circ}(R)$ and $E_{1/2}^{\circ}(L)$ are the standard reduction potentials for the right-hand and left-hand half-cells, F is the Faraday constant, and n is the number of electrons involved in the cell reaction (concentrations are used instead of activities). By measuring the effect on E of changes in the concentrations of different substances, one can ascertain which substances are involved in the cell reaction and determine their stoichiometric coefficients.

The cells studied consisted of Cu and Zn dipping into dilute hydrochloric acid solutions at 21 °C; E was measured by connecting a voltmeter across the metal leads while the solution was stirred. To examine the effect of varying $[Zn^{2+}]$, we dissolved a weighed amount of $ZnCl_2$ or $ZnSO_4$ in a measured volume of HCl solution and added measured amounts of the resulting solution from a buret to a measured volume of the original HCl solution. By inserting Zn and Cu electrodes into the solution, we could measure how the emf ($V_{Cu} - V_{Zn}$) changed as $[Zn^{2+}]$ changed with $[H^+]$ re-

Table 1. Measured Potentials of Different Lemon Cells Compared with Difference of Reduction Potentials

Metal on Right	Metal on Left	$(V_{right} - V_{left})$ /V	$(E_{1/2}^{\circ}(r) - E_{1/2}^{\circ}(l))$/ V [a]
Cu^{2+}/Cu	Pb^{2+}/Pb	0.433	0.461
Cu^{2+}/Cu	Zn^{2+}/Zn	0.914	1.103
Cu^{2+}/Cu	Ni^{2+}/Ni	0.182	0.570
Cu^{2+}/Cu	Fe^{2+}/Fe	0.398	0.749
Pb^{2+}/Pb	Zn^{2+}/Zn	0.528	0.637
Pb^{2+}/Pb	Ni^{2+}/Ni	-0.417	0.104
Pb^{2+}/Pb	Fe^{2+}/Fe	-0.007	0.283
Ni^{2+}/Ni	Zn^{2+}/Zn	0.933	0.533
Fe^{2+}/Fe	Zn^{2+}/Zn	0.517	0.354
Ni^{2+}/Ni	Fe^{2+}/Fe	0.429	0.179

[a]Standard half-cell reduction potentials from Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980. These values are for 25 °C, whereas our measurements were made at 21 °C.

maining constant. Data from two runs are shown in Figure 1. The fact that the emf decreases with $[Zn^{2+}]$ shows that Zn^{2+} is a product of the cell reaction. From the $ZnSO_4$ experiment, fitting emf versus $\ln[Zn^{2+}]$ to a line (r^2 = .985) yields a slope of -0.0130 ± 0.0008; since RT/F = 0.025310 at 21 °C, this corresponds to $n = 1.95 \pm 0.12$. For the $ZnCl_2$ data set, the slope (r^2 = .982) is -0.0136 ± 0.0008, so that $n = 1.86 \pm 0.10$. This shows that the oxidation half-cell is $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$.

Similar experiments showed that varying the concentration of Cu^{2+} has no effect on the emf. Thus reduction of Cu^{2+} to Cu is not the other half-cell (nor could it be, since there is very little Cu^{2+} present in the hydrochloric acid). It has already been remarked that the copper can be replaced by other materials, so that it is just an "electron shunt" (1). The reduction half-cell must therefore involve other substances present in solution. Two obvious choices are the reduction of dissolved O_2 to water and the reduction of H^+ to H_2. The standard reduction potential for $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ is 1.2210 V (5), and that for $2H^+ + 2e^- \rightarrow H_2$ is of course 0.00 V. Since $E_{1/2}$ for Zn is -0.86 V and the Zn/Cu lemon cell has an emf near 1.0 V, the H^+ reduction is a better candidate. As both reactions involve one electron per hydrogen ion, Nernst equation measurements cannot distinguish between them (although they can rule them both out if the slope of a plot of emf versus pH does not correspond to $n = 1$). The choice is made below on the basis of experimental evidence.

In fact, the measured emf as a function of pH is linear only for pH > ~3.8. As the pH decreases below 3.8, the emf rises rapidly and goes through a maximum value of about 1.0 V near pH 3.4. This behavior may be related to the dissolution of Zn, which becomes appreciable at lower pH values. The Zn dissolution means that the lemon cell is not at thermodynamic equilibrium at open circuit; it is inherently irreversible, as has long been understood (6, p 164). The Nernst equation can be used if the rate of dissolution is so small that it can be neglected. Fortunately, one can go to pH much higher than 3, even into basic solutions. The measured emf was 0.90 V for HCl at pH 3.20, 0.81 V for HCl at pH
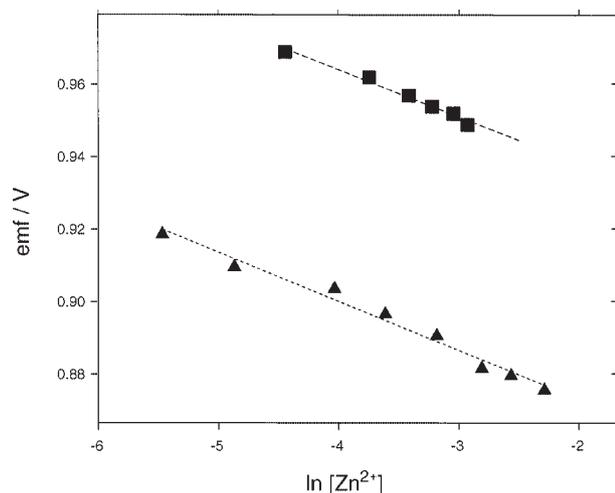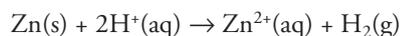
4.10, 0.64 V for distilled water at pH 6.23, and 0.42 V for KOH solution with calculated pH 10.45. Fitting these four values to a line gives a slope of -0.0648 ± 0.0061, corresponding to $n = 0.900 \pm 0.087$ or 1.

Our measurements thus suggest that the cell reaction in the lemon cell, with Cu on the right, is

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

The standard emf for this cell would be the negative of the half-cell reduction potential of Zn, that is, 0.86 V. The actual emf depends on the concentrations of Zn^{2+} and H^+, according to the Nernst equation. When the cell is allowed to operate by electrically connecting the Zn and Cu electrodes, gas bubbles are observed at both electrodes. The *production* of gas confirms that H^+ rather than O_2 is reduced. The bubbles, which are larger and more numerous on the Cu than on the Zn, are hydrogen.

Discussion

Since at open circuit the Cu is at higher electrical potential than the Zn, closing the circuit leads to positive current flow in the external circuit from the Cu to the Zn, electrons flowing in the opposite direction. At the Zn electrode, Zn atoms are converted to Zn^{2+} ions in solution, leaving electrons behind on the electrode. (Simultaneously, some Zn may dissolve to Zn^{2+}, reducing H^+ to H_2, but this does not contribute to the cell reaction or the current). The Zn^{2+} ions, along with H^+ ions, migrate through the solution from the Zn to the Cu electrode; negative ions (chloride or citrate) migrate in the opposite direction. Thus positive current flows from Zn to Cu in solution.

At the Cu electrode, H^+ ions are reduced to H_2 gas. The electrons responsible for the reduction of H^+ come from the Zn, which is consistent with a flow of electrons in the external circuit from Zn to Cu. Loss of electrons by the Zn must be accompanied by dissolution of Zn^{2+}. Weighing the electrodes before and after running the cell shows that the Zn electrode loses mass but the Cu electrode does not. The orange juice cell operates similarly, with Mg replacing Zn, as discussed by Kelter et al. (2).

At open circuit, there is very little loss of Zn if the pH is not too low. It has long been known that Zn dissolves very slowly in dilute acid, but that the reaction is speeded up by minute amounts of Cu^{2+} salts, which form copper particles on the Zn surface (7, p 452). The reason for the slow rate is that Zn is a poor adsorber of hydrogen atoms, and the first step in the reduction of H_3O^+ to H_2 is its reduction to adsorbed H (8, Section IV.G.2). For the orange juice cell, Kelter et al. measured and compared the rates of dissolution of Mg at open circuit and when the cell is operating. The dissolution of Mg in orange juice is appreciable, unlike Zn in dilute acid; and the reduction of H^+ to H_2 at the Mg electrode, which accompanies dissolution of Mg, does not contribute to the Faradaic current (2).

The cell may also be understood by noting that Zn is a more active metal (better reducing agent) than Cu, so its electrons have a higher Gibbs free energy (more correctly, electrochemical potential [9]). Thus, if the two metals are placed in electrical contact, electrons flow from the more active (Zn) to the less active (Cu) until equilibrium is reached and

Figure 1. Measured emf's of simulated lemon cells (Cu and Zn electrodes dipping into HCl solution) as a function of Zn^{2+} concentration. (■) $ZnSO_4$; (▲) $ZnCl_2$. Least-square linear fits are shown as dashed lines.

the electrochemical potential of electrons is the same in both metals. The Zn is then charged positively and the Cu negatively, the difference in electrical potential being the "contact potential" (*8*, pp 11, 183). Since electrons have a negative charge, the charging raises the Gibbs free energy of electrons in the Cu. It becomes high enough for them to reduce hydrogen ions in solution to H_2. If another inactive metal were used instead of copper, the cell would operate in the same way and with the same open-circuit potential.

We replaced the lemon in the lemon cell by an electrolytic solution in a beaker. The beaker can in turn be replaced by a porous material such as cloth impregnated with electrolyte. Several such cells in series form a voltaic pile, except that Volta used silver instead of copper (*6*, p 36; *10*, p 114). (It has long been known that during the operation of this cell Zn dissolves and H_2 is generated at the silver electrode [*6*, p 164].) By piling up more than 30 Ag–cloth–Zn cells, Volta was able to generate a high voltage (*10*, p 114). Aside from creating sparks, the voltaic pile made it possible to study the chemical effects of electric current, such as the electrolytic decomposition of water (*7*, p 20; *10*, p 114), observed just four years after the invention of the pile. Subsequently, Volta replaced his pile by a "crown of cups", each cup being a cell like the ones we have studied. By measuring cells made with different metals, Volta generated the first electrochemical series (*6*, p 164; *7*, p 20). Having no voltmeter, he measured the cell emf by the intensity of "sensation of taste and light" generated by touching the leads to his tongue (*10*, p 51). The historical significance of the voltaic pile adds to the importance of understanding how the lemon cell works; I hope our observations are useful toward this end.

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