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Joule heating rate need not equal I^2R, where R is the Ohmic resistance: The case of voltaic cells

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The electrolyte within a charging or discharging voltaic cell, carrying current I, has time-dependent carrier densities. Therefore the energy conservation argument that equates the total rate of Joule heating $\mathcal{P}$ to the rate of decrease of electrical energy is inappropriate because it neglects changes in chemical energy. Explicit study of two systems (the lead-acid cell and the Zn-Cu cell) shows that the Joule heating resistance $R_J = \mathcal{P}/I^2$ differs from the Ohmic resistance $R = \Delta V/I$ (ΔV is the voltage drop across the electrolyte). R/R_J can be greater than or less than unity. R_J involves only the current-carrying ions, whereas R involves *all* of the ions.
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INTRODUCTION

Despite its nearly two hundred year-old history, electrochemistry is an area which still yields suprises [1]. For example, it is usually assumed that even when current I flows through it, the electrolyte within a voltaic cell is *locally electroneutral* [2,3]. However, it was recently predicted that, for a well-charged lead-acid cell under slow, steady discharge (i.e., the linear regime) the voltage profile is quadratic in space [4]. This implies a uniform charge density within the bulk of the electrolyte. Indeed, about half of the voltage drop ΔV across the electrolyte is due to this charge, over and above the voltage drop due to resistive effects. We have recently observed a quadratic voltage profile [5].

It is also usually assumed that the Joule heating resistance R_J, determined from the total rate of Joule heating $\mathcal{P}$ of the electrolyte via $R_J = \mathcal{P}/I^2$, is the same as the Ohmic resistance R, determined from $R = \Delta V/I$. In the present work we show that, in general, one should expect that $R_J \neq R$, and we demonstrate this explicitly for two types of voltaic cells. This difference has significant consequences because it means that, in energy accounting associated with voltaic cells, one can make serious errors in estimating the rate of heat production by using the Ohmic resistance R. Note that R/R_J can be either greater than or less than unity, so that one can both overestimate or underestimate the rate of heating by using R. Although R_J must be positive, R can have either sign [6].

For a charging or discharging voltaic cell, the electrolyte has time-dependent carrier densities. This is because the electrochemical reactions at the electrode-electrolyte interfaces cause ion flux to or from the electrodes. Therefore the energy conservation argument that equates the total rate of Joule heating $\mathcal{P}$ to the rate of decrease of electrical energy is inappropriate because it neglects changes in chemical energy. Note that the chemical energy in the cell dominates the electrical energy and the Joule heating, and to include the full electrochemical reaction one must also include the properties of the electrode. This is unnecessary for the calculation of $\mathcal{P}$, which is a property only of the electrolyte.

RATE OF JOULE HEATING

Having established that one should expect $R_J \neq R$, and since it is already known that $R = \Delta V/I$ involves only a straightforward calculation of ΔV, we now indicate how to obtain the total rate of Joule heating $\mathcal{P}$, which determines $R_J = \mathcal{P}/I^2$. This may be obtained either directly or by a generalization of Refs. [7–9], which study the rate of heating per unit volume of a multicomponent fluid in the absence of electrical effects. We can obtain the desired result from these works by neglecting convection, assuming uniform temperature, and generalizing the chemical potential μ_i of the ith ion (of charge ez_i, number density n_i, and number flux density j_i). Thus, we replace μ_i by the electrochemical potential $\tilde{\mu}_i = \mu_i + ez_iV$, where V is the electrical potential. The local rate of heating per unit volume, as usual, is the sum of products of fluxes times thermodynamic forces. Here, the fluxes are the j_i's and the thermodynamic forces are the $-\partial_x\tilde{\mu}_i \equiv (ez_iE_i)$'s. For our two-component system we then have

$$p = -j_1\frac{\partial\tilde{\mu}_1}{\partial x} - j_2\frac{\partial\tilde{\mu}_2}{\partial x} = J_1\frac{\partial E_1}{\partial x} + J_2\frac{\partial E_2}{\partial x} \approx \frac{J_1^2}{\sigma_1} + \frac{J_2^2}{\sigma_2}, \tag{1}$$

$$\tilde{\mu}_i = \mu_i + ez_iV, \quad J_i = ez_ij_i, \quad E_i = -\partial_x\tilde{\mu}_i ez_i.$$

Here σ_i is the electrical conductivity. In taking $J_i \approx \sigma_iE_i$, we neglect cross coupling (i.e., a nonzero E_2 does not cause a J_1, and vice versa).

IONIC FLUX FOR SLOW, STEADY DISCHARGE

We will apply Eq. (1) explicitly to two systems in the slow, steady discharge regime: the lead-acid cell and the Zn-Cu cell. First, however, we will need the partial electric current densities, J_1 and J_2.

In Ref. [4] we argued that, under slow, steady discharge, diffusion has enough time to nearly even out any nonuniformities associated with molecules being consumed or produced at the electrodes. Hence the electrolyte is depleted at a uniform rate throughout the system: for the ith molecule, ∂_tn_i is constant in space. We now use this in the continuity equation for the ith molecule, with no chemical reactions,

$$0 = \partial_tn_i + \partial_xj_{n_i}. \tag{2}$$

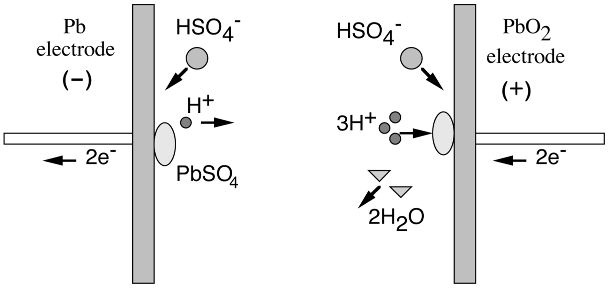

FIG. 1. Chemical reactions at the Pb and PbO_2 interfaces for a well-charged lead-acid cell. Both reactions produce $PbSO_4$, with consumption of the ions constituting H_2SO_4 and production of H_2O.

Since $\partial_t n_i$ is constant in space, Eq. (2) implies that the slope of the associated ionic flux is constant in space. Since the ionic fluxes are known at the electrodes (being determined by the electrochemical reactions at the electrodes), each ionic flux within the electrolyte is determined by drawing a straight line between its values at the electrodes.

THE LEAD-ACID CELL

Consider a well-charged lead-acid cell whose Pb electrode is at $x=0$ and whose $PbSO_4$ electrode is at $x=d$, as in Fig. 1. In applying Eq. (1), we let species number 1 correspond to H^+ (H, for short) and species number 2 correspond to $HSO_4{}^-$ (S, for short), so that $\sigma_1=\sigma_H$, $\sigma_2=\sigma_S$, $z_1=z_H=1$, and $z_2=z_S=-1$. The diffusion coefficients take on the values $D_H=9.3\times10^{-5}\,\mathrm{cm^2/sec}$, and $D_S=1.3\times10^{-5}\,\mathrm{cm^2/sec}$ [3]. The conductivities can then be obtained via the Einstein relations, expressed as

$$F_i\equiv\frac{ez_iD_i}{\sigma_i}=\frac{1}{ez_i}\frac{\partial\mu_i}{\partial n_i}\approx\frac{k_BT}{en_i}. \tag{3}$$

Note that, on average, $n_H=n_S$ (so $F_S\approx F_H$) although there will be small gradients proportional to the current I [4].

The chemical reactions at the electrodes impose boundary conditions on the H^+ and $HSO_4{}^-$ ionic fluxes. From Fig. 1 we can determine these boundary conditions, and then, by the linear interpolation argument given above, the ionic flux profiles. We have [4]

$$j_H(x)=j_0\left(1+2\frac{x}{d}\right),\quad j_S(x)=j_0\left(-1+2\frac{x}{d}\right). \tag{4}$$

(See Fig. 2.) Note that the total current density $J=ej_H-ej_S=e2j_0$ is constant in space, and that $I=JA=2ej_0A$. Placing Eq. (4) in Eq. (1), the local rate of heating becomes

$$\begin{aligned}p&=\frac{J_H^2}{\sigma_H}+\frac{J_S^2}{\sigma_S}\\&=\frac{e^2j_0^2}{\sigma_H}\left[1+4\left(\frac{x}{d}\right)+4\left(\frac{x}{d}\right)^2\right]+\frac{e^2j_0^2}{\sigma_S}\left[1-4\left(\frac{x}{d}\right)+4\left(\frac{x}{d}\right)^2\right].\end{aligned} \tag{5}$$

We plot this in Fig. 3, in units of $e^2j_0^2/\sigma_H$. Clearly, it is nonuniform, unlike the rate of heating in a uniform wire with only a single charge-carrier.

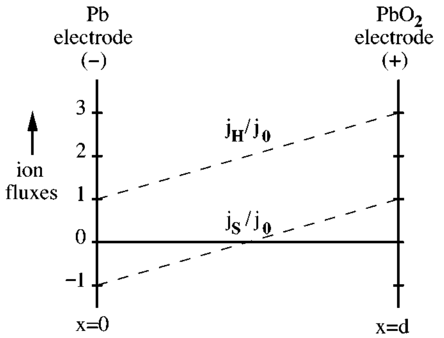

FIG. 2. Ionic fluxes within the well-charged lead-acid cell under slow, steady discharge. Both electrodes consume $HSO_4{}^-$ ions.

Integrating over the area A and over x from 0 to d, the total rate of heating is

$$\mathcal{P}=\int p\,dV=e^2Aj_0^2d\left(\frac{13}{3\sigma_H}+\frac{1}{3\sigma_S}\right)=\frac{e^2I^2d}{4A}\left(\frac{13}{3\sigma_H}+\frac{1}{3\sigma_S}\right). \tag{6}$$

Equating Eq. (6) to I^2R_J yields

$$R_J=\frac{e^2d}{A}\left(\frac{13}{12\sigma_H}+\frac{1}{12\sigma_S}\right)=e^2\frac{d}{\sigma_HA}\left(\frac{13}{12}+\frac{\sigma_H}{12\sigma_S}\right). \tag{7}$$

By Eq. (3), $(13/12)+(\sigma_H/12\sigma_S)\approx(13/12)+(D_H/12D_S)\approx1.68$; recall that $n_H\approx n_S$.

To obtain R, note that Ref. [3] finds the voltage profile

$$\begin{aligned}V(x)-V(0)=&-\frac{j_0/d}{F_S^{-1}+F_H^{-1}}\\&\times\left[\left(\frac{1}{D_H}-\frac{1}{D_S}\right)x^2+\left(\frac{1}{D_H}+\frac{1}{D_S}\right)xd\right].\end{aligned} \tag{8}$$

It is plotted in Fig. 4; note the minimum. From Eq. (8), we obtain the Ohmic resistance

$$R=\frac{|\Delta V|}{I}=\frac{|V(d)-V(0)|}{I}=\frac{1}{F_S/F_H+1}\frac{d}{\sigma_HA}, \tag{9}$$

or

$$R=\frac{d}{\tilde{\sigma}A},\quad \tilde{\sigma}=\sigma_H+\sigma_S(D_H/D_S). \tag{10}$$

Note that $(F_S/F_S+1)^{-1}\approx0.5$.

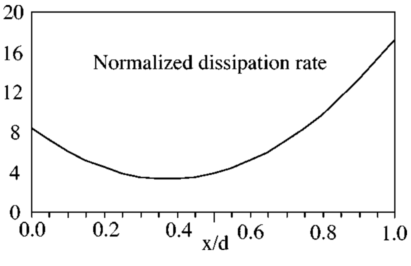

FIG. 3. Profile of the dissipation rate, in units of $e^2j_0^2/\sigma_H$, associated with the lead-acid cell under slow, steady discharge.

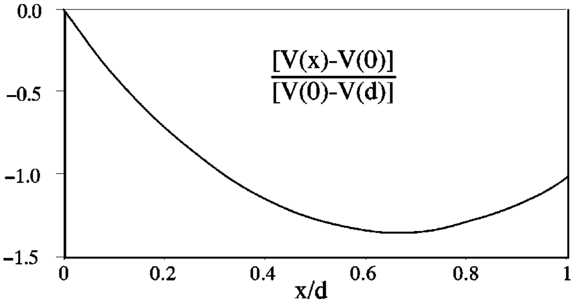

FIG. 4. Normalized voltage profile associated with the well-charged lead-acid cell under slow, steady discharge.

A comparison of Eqs. (7) and (10) yields that $R_J \approx 3.4R$. As indicated from general arguments, the Joule resistance differs from the Ohmic resistance.

THE Zn-Cu CELL

Now consider a system with Zn and Cu electrodes and a dilute electrolyte that includes both $ZnSO_4$ and $CuSO_4$. The electrolyte contains Cu^{2+}, Zn^{2+}, and $SO_4{}^{2-}$ ions, subject to the constraint that the number of $SO_4{}^{2-}$ ions (denoted S) equals the sum of the Cu^{2+} and Zn^{2+} ions. The diffusion constants take the values $D_{\mathrm{Cu}} = 0.72 \times 10^{-5}$ cm^2/sec, $D_{\mathrm{Zn}} = 0.71 \times 10^{-5}$ cm^2/sec, and $D_{\mathrm{SO}_4} = 1.065 \times 10^{-5}$ cm^2/sec [3]. Note that $D_{\mathrm{Cu}} \approx D_{\mathrm{Zn}}$. The concentrations of Cu^{2+} and Zn^{2+} typically differ. Hence, σ_{Cu} and σ_{Zn} differ, as do F_{Cu} and F_{Zn}.

The Zn goes into solution as Zn^{2+} with flux j_0, depositing two electrons on the Zn electrode, taken to be at $x = 0$. The Cu^{2+} goes out of solution as Cu with flux j_0, absorbing two electrons from the Cu electrode, taken to be at $x = d$. In steady state, the $SO_4{}^{2-}$ does not flow to or from either electrode. From the discussion above, for slow, steady discharge the fluxes at all positions are determined by drawing a straight line between their values at the electrodes:

$$j_{\mathrm{Zn}} = j_0\left(1 - \frac{x}{d}\right), \quad j_{\mathrm{Cu}} = j_0\frac{x}{d}, \quad j_{\mathrm{S}} = 0. \tag{11}$$

With all valences z_i set to magnitude 2 in Eq. (1), integrating Eq. (11) over the voltaic cell gives for the total rate of Joule heating

$$\mathcal{P} = \frac{I^2 d}{3A}\left(\frac{1}{\sigma_{\mathrm{Cu}}} + \frac{1}{\sigma_{\mathrm{Zn}}}\right), \quad I = 2ej_0A. \tag{12}$$

By $\mathcal{P} = I^2R_J$, this leads to

$$R_J = \frac{d}{3A}\left(\frac{1}{\sigma_{\mathrm{Cu}}} + \frac{1}{\sigma_{\mathrm{Zn}}}\right). \tag{13}$$

Note that the $SO_4{}^{2-}$ do not contribute to R_J, since they carry no current. Nevertheless, they affect the system's electrical properties, and therefore they contribute to the Ohmic resistance $R = \Delta V/I$. This is because there is an electric field within the cell, and that field is affected by the sulfate ion. We now determine that electric field and the associated ΔV.

There are seven unknowns: E, three ionic fluxes, and three ionic densities. Three equations for the ionic fluxes are given in Eq. (11). There are also four equations to determine E and the three ionic densities. One is Gauss's Law in one dimension,

$$\partial_x E = \frac{4\pi k}{\kappa}\rho = \frac{4\pi k}{\kappa}(2e)(n_{\mathrm{Zn}} + n_{\mathrm{Cu}} - n_{\mathrm{S}}). \tag{14}$$

Here $k = (4\pi\epsilon_0)^{-1} \approx 9.0 \times 10^9$ N-m^2/C^2 in SI units, and $\kappa \approx 78$ is the relative electric permeability of the water solution. The other three equations are the constitutive relations, equivalent to $J_i = \sigma_i E_i$, given by

$$\begin{aligned} 2e\vec{j}_{\mathrm{Cu}} &= \sigma_{\mathrm{Cu}}\vec{E} - 2eD_{\mathrm{Cu}}\vec{\nabla}n_{\mathrm{Cu}}, \\ 2e\vec{j}_{\mathrm{Zn}} &= \sigma_{\mathrm{Zn}}\vec{E} - 2eD_{\mathrm{Zn}}\vec{\nabla}n_{\mathrm{Zn}}, \\ -2e\vec{j}_{\mathrm{S}} &= \sigma_{\mathrm{S}}\vec{E} + 2eD_{\mathrm{S}}\vec{\nabla}n_{\mathrm{S}}. \end{aligned} \tag{15}$$

These equations are solved by taking the x derivative of Eq. (14), and then using Eq. (15) to eliminate the unknown density gradients in terms of the known fluxes and the unknown electric field. This leads to

$$\partial_x^2 E = \frac{1}{\lambda^2}E - \frac{8\pi k e}{\kappa}\left(\frac{j_{\mathrm{Cu}}}{D_{\mathrm{Cu}}} + \frac{j_{\mathrm{Zn}}}{D_{\mathrm{Zn}}} - \frac{j_{\mathrm{S}}}{D_{\mathrm{S}}}\right), \tag{16}$$

where the Debye-Hückel screening length λ is given by

$$\frac{1}{\lambda^2} = \frac{4\pi k}{\kappa}\left(\frac{\sigma_{\mathrm{Cu}}}{D_{\mathrm{Cu}}} + \frac{\sigma_{\mathrm{Zn}}}{D_{\mathrm{Zn}}} + \frac{\sigma_{\mathrm{S}}}{D_{\mathrm{S}}}\right). \tag{17}$$

In general, $\lambda^{-2} = (4\pi k/\kappa)\Sigma_i(\sigma_i/D_i)$.

To solve Eq. (16), let us assume that $\partial_x^2 E = 0$. (This is equivalent to assuming zero gradient for the net charge density.) Then

$$E = 2e\frac{j_{\mathrm{Cu}}/D_{\mathrm{Cu}} + j_{\mathrm{Zn}}/D_{\mathrm{Zn}} - j_{\mathrm{S}}/D_{\mathrm{S}}}{\sigma_{\mathrm{Cu}}/D_{\mathrm{Cu}} + \sigma_{\mathrm{Zn}}/D_{\mathrm{Zn}} + \sigma_{\mathrm{S}}/D_{\mathrm{S}}}. \tag{18}$$

In general, $E = e(\Sigma_i z_i j_i/D_i)/(\Sigma_i \sigma_i/D_i)$.

Since, by Eq. (11), the ionic fluxes vary linearly in space (or are zero), Eq. (18) gives an E that, at most, varies linearly in space, consistent with the assumption that $\partial_x^2 E = 0$. Explicitly substituting Eq. (11) into Eq. (18), and setting $D_{\mathrm{Cu}} \approx D_{\mathrm{Zn}}$, we find that

$$E \approx \frac{2ej_0}{\tilde{\sigma}}, \quad \tilde{\sigma} = \sigma_{\mathrm{Cu}} + \sigma_{\mathrm{Zn}} + \sigma_{\mathrm{S}}(D_{\mathrm{Zn}}/D_{\mathrm{S}}). \tag{19}$$

This is constant in space, so

$$\Delta V \approx Ed = \frac{2edj_0}{\tilde{\sigma}}. \tag{20}$$

From Eqs. (20) and (12), the Ohmic resistance $R = \Delta V/I$ is

$$R = \frac{d}{\tilde{\sigma}A}, \quad \tilde{\sigma} = \sigma_{\mathrm{Cu}} + \sigma_{\mathrm{Zn}} + \sigma_{\mathrm{S}}(D_{\mathrm{Zn}}/D_{\mathrm{S}}). \tag{21}$$

A comparison with Eq. (13) shows that $R \neq R_J$. Note that R_J is independent of the sulfate ion concentration n_{S}, whereas R depends upon n_{S}. Also note that, as usually assumed without proof, E is uniform in space (in contrast to the case for the lead-acid cell). Nevertheless, $R_J \neq R$.

Equations (15) and (18) can be employed to obtain the ionic density gradients. One can then verify explicitly that Eq. (18) and these ionic density gradients give zero gradient of the total charge density. If the Cu and Zn diffusion constants are not set equal to one another, then there is a small linear variation in E, and hence (by Gauss's Law) a small uniform charge density in the bulk. As discussed in Ref. [4], any bulk charge density is cancelled out at the electrodes by the charge associated with the surfaces. [Surface solutions are also known as solutions to the homogeneous, or source-free equations, obtained from Eq. (16) with the ionic current densities set to zero.]

SUMMARY AND DISCUSSION

We have shown, with two specific examples, that for slow, steady discharge of a voltaic cell, the Joule resistance $R_J = \mathcal{P}/I^2$ is different than the Ohmic resistance $R = \Delta V/I$. The reason for the breakdown of the usual argument for $R_J = R$ (that the loss in electrical potential energy should equal the rate of Joule heating) is that, because of ion flow, the ionic number densities are changing. Note that R_J involves only the current-carrying ions, whereas R involves *all* of the ions, current-carrying or not. This is because the rate of Joule heating, and thus R_J, involves the squares of the ionic currents, whereas the voltage across the electrolyte, and thus R, involves the electric field, to which *all* ions contribute.

As a check, note the following. If both ionic currents were uniform, by the continuity equation their densities would be uniform, so there would be no diffusion terms driving the ionic currents. Hence, the ionic currents would be driven only by the electric field, which would be uniform. Then $I = JA = \sigma EA$, where $\sigma = \sigma_1 + \sigma_2$, so $R = \Delta V/I = Ed/\sigma EA = d/\sigma A$. Moreover, in the absence of diffusion, $e^2 j_1^2/\sigma_1 = \sigma_1 E^2$ and $e^2 j_1^2/\sigma_1 = \sigma_1 E^2$, so $\mathcal{P} = Ad(\sigma_1 + \sigma_2)E^2 = Ad\sigma E^2 = (d/\sigma A)I^2$, from which $R_J = d/\sigma A$. Hence, when the current densities are uniform across the voltaic cell, $R_J = R$. This relation also holds when there is a single charge carrier, such as: electrons in a wire, Cu^{2+} ions in a Cu-Cu cell with $CuSO_4$ electrolyte, driven by an external power source; or Li^+ ions in many modern voltaic cells, where Li is in different chemical combinations on the two electrodes, and the electrolyte contains an ionized lithium salt. Extending beyond the steady-state considerations of the present work, the dynamical response of multiple-charge-carrier systems can also be expected to yield different values for the Joule and Ohmic resistances.

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[1] Chemists are interested primarily in the chemical phenomena that occur at the electrode-electrolyte interface, whereas the present work is concerned with the properties of the electrolyte itself. Hence, chemists measure the nonzero voltage drops V_1 and V_2 between each electrode and the electrolyte. This is nonzero even without current flow; current flow modifies this voltage drop, and causes a voltage drop ΔV across the electrolyte. It is ΔV that is our present concern.

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