

The Lead–Acid Battery: Its Voltage in Theory and in Practice

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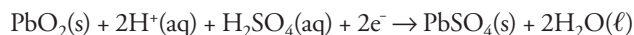
The lead–acid storage battery is the most widely used rechargeable power source in the world today. It certainly is well known to anyone who owns and maintains an automobile. General chemistry textbooks typically discuss the battery but limit their coverage to a description of its components and the reactions occurring at its electrodes. In this article we expand that coverage by asking a very practical question: How does the voltage of the battery depend upon the state of its charge or discharge? The question is addressed theoretically by use of the Nernst equation and practically by reference to actual battery performance. As we uncover the details of this popular electrochemical device, we will improve our understanding of such fundamental concepts as standard states, activity coefficients, and electrode overvoltage.

Lead–Acid Battery Fundamentals

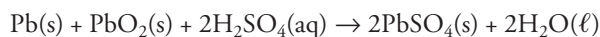
The common 12-volt automobile battery consists of six individual cells connected in series so that the total voltage generated is six times that of each cell. Figure 1 illustrates a single cell at two stages of its life cycle. Its electrodes are metal plates of lead constructed in the form of grids to maximize their surface area. The electrodes are immersed in an electrolyte of aqueous sulfuric acid. As shown on the top of the figure, the cell is fully charged and acting as a galvanic cell to supply electrical current to an external load. During this process the lead anode is oxidized to lead(II) sulfate, an insoluble white solid, by the half reaction



The anode has a negative charge because it produces electrons. The cathode consists of lead(IV) oxide deposited on a lead plate. During discharge the red-brown oxide is reduced to lead(II) sulfate by the reaction



The cathode has a positive charge because electrons are consumed there. The two half-reactions can be combined to give the overall discharge reaction



Sulfuric acid is consumed and water is produced in the reaction. Hence, both the concentration and the density of the electrolyte drop steadily during discharge. The state of charge of a lead–acid battery can be conveniently determined by measuring the specific gravity of its electrolyte.

The cell is shown fully discharged on the bottom of Figure 1. Its two electrodes now have lead(II) sulfate deposited on their grids. It is acting as an electrolytic cell while it is recharged by an external power source. With the electrical current forced to flow in the opposite direction, the reactions described above are reversed and the acid concentration steadily increases. During charging the former anode functions as a cathode, and vice versa. This change in roles occurs with any rechargeable cell. Electrochemical engineers avoid confusion

by referring to the electrodes as *negative* or *positive*. These designations do not change when the cell switches functions.

Cell Voltage and the Nernst Equation

Electrochemical theory can predict how the voltage of a lead–acid cell changes with the concentration of its electrolyte, but the process is not simple. It is complicated by the fact that sulfuric acid is a nonideal solute. It is present in the cell at high concentrations where its activity differs greatly from the ideal behavior used to define its standard state. A further complication results because water is a participant in the cell reaction as well as the solvent for the acid. Mindful of these factors, we will now calculate the cell voltage as a function of its acid concentration. Two theoretical models will be developed which treat the matter of nonideality in different fashion.

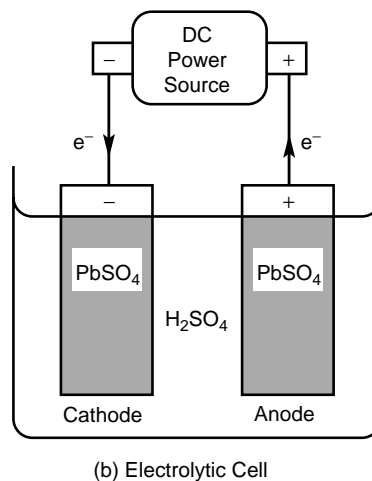
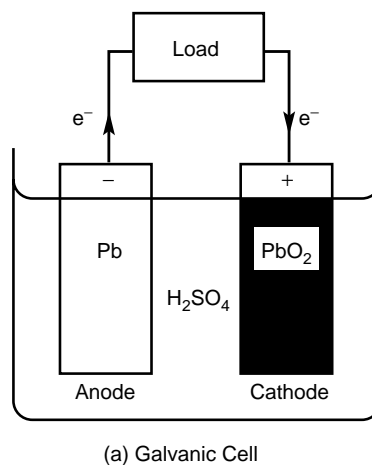


Figure 1. Two stages of a lead–acid cell: (a) fully charged and supplying current to an external load and (b) fully discharged and receiving current from an external power source.

Approximate Model

The first model is approximate in that it allows simplifying assumptions. The sulfuric acid in the electrolyte is assumed to be a strong monoprotic acid completely dissociated into H^+ and HSO_4^- . In the interest of simplicity, the fact that HSO_4^- is itself a weak acid is not considered. The overall cell discharge reaction is thus written



to show each substance in the form which the model regards to be its standard state.

The standard free-energy change for the reaction can be calculated in usual fashion from

$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants}) \quad (1)$$

where ΔG_f° is the standard free-energy of formation of each species. Using data from the literature (1) as listed in Table 1, we find that $\Delta G^\circ = -371.1$ kJ at 298.15 K. The standard voltage, or electromotive force, of the cell can then be obtained from the relationship

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad (2)$$

where $n = 2$ mol for this reaction and Faraday's constant, F , equals 96,485 C/mol. The result is $E_{\text{cell}}^\circ = 1.92$ volts for this model.

The voltage at conditions other than the standard state can be determined from the Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - (RT/nF) \ln Q \quad (3)$$

where the reaction quotient Q contains the activities of all species in the reaction. In general, the *activity* of a species is a dimensionless quantity that adjusts for the fact that the species may not be present in its standard state. The activity can be regarded as the effective concentration of the species relative to its standard-state concentration. To apply the Nernst equation we must express the activity of each species in the cell reaction.

The standard state of a liquid or solid is defined as the pure substance itself. The Pb, PbO_2 , and PbSO_4 in our cell meet this requirement. Hence, their activities are constant and equal to 1. Thus

$$a_{\text{Pb}} = a_{\text{PbO}_2} = a_{\text{PbSO}_4} = 1$$

The H_2O in the cell is not pure, since it contains dissolved sulfuric acid. Although water is not in its standard state, the approximate model assumes its activity is unaffected by the solute. Hence, we write

$$a_{\text{H}_2\text{O}} = 1$$

Finally, we must assign activities to the H^+ and HSO_4^- ions in the reaction. The standard state of a solute is by definition an ideal solution whose concentration is 1 mole per kilogram of solvent. In other words, it is the hypothetical condition the solute would reach if the activity it displays at infinite dilution could be increased in proportion to its concentration until that concentration reaches 1 molal. The approximate model assumes the two ions behave ideally. Hence, their activities are

$$a_{\text{H}^+} = \frac{m_{\text{H}^+}}{m^\circ} \quad \text{and} \quad a_{\text{HSO}_4^-} = \frac{m_{\text{HSO}_4^-}}{m^\circ}$$

Table 1. Thermodynamic Properties of Pure Substances and Aqueous Ions at 298.15 K

Substance	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\Delta G_f^\circ/\text{kJ mol}^{-1}$	$S^\circ/\text{J mol}^{-1} \text{K}^{-1}$
Pure Substances			
Pb(s)	0.0	0.0	64.8
$\text{PbO}_2(\text{s})$	-277.4	-217.3	68.6
$\text{PbSO}_4(\text{s})$	-920.0	-813.0	148.5
$\text{H}_2\text{O}(\ell)$	-285.8	-237.1	70.0
Aqueous Ions			
$\text{H}^+(\text{aq})$	0.0	0.0	0.0
$\text{HSO}_4^-(\text{aq})$	-887.3	-755.9	131.8
$\text{SO}_4^{2-}(\text{aq})$	-909.3	-744.5	20.1

where m_{H^+} and $m_{\text{HSO}_4^-}$ are the molalities of the ions, and m° is the standard concentration of 1 molal.

All activities have now been assigned and Q can be written

$$Q = \frac{1}{(a_{\text{H}^+})^2 (a_{\text{HSO}_4^-})^2}$$

Those activities that are fixed at 1 need not be included in the equation. Upon insertion of the activity expressions we obtain

$$Q = \frac{(m^\circ)^4}{(m_{\text{H}^+})^2 (m_{\text{HSO}_4^-})^2}$$

Substitution of this expression into the Nernst equation enables us to calculate the voltage of a lead-acid cell having any acid concentration. For example, consider a cell whose electrolyte is 0.1 molal H_2SO_4 . Since the model takes H_2SO_4 to be a strong monoprotic acid, we have $m_{\text{H}^+} = 0.1$ molal and $m_{\text{HSO}_4^-} = 0.1$ molal. These values give $Q = 1 \times 10^4$. Finally, we obtain $E_{\text{cell}} = 1.80$ volts by substitution into the Nernst equation.¹ The cell in this example understandably delivers less voltage than the standard cell because its acid concentration is lower.

Using the method illustrated above, E_{cell} can be calculated as a function of sulfuric acid concentration. Figure 2 displays the results of such calculations using two different styles of presentation. Graph 2a shows cell voltage versus log of the acid concentration. The relationship is linear, as should be expected from the form of the Nernst equation. In graph 2b the acid concentration is plotted linearly and descending from 6 molal. This initial concentration is typical of a freshly charged lead-acid battery. The graph shows the gradual decline of cell voltage through the battery lifetime.

Rigorous Model

The second model is more rigorous in that it does not rely upon approximations. It acknowledges that sulfuric acid is diprotic and able to dissociate fully into 2H^+ and SO_4^{2-} . The overall cell reaction is written in the style



to show each substance in the form that the model defines as its standard state. Of course, sulfuric acid achieves the full dissociation shown only at infinite dilution. Thus, the standard state assigned to it by this model is purely hypothetical. In recognition of that fact we must not assume that the ions behave ideally.

Application of eq 1 and the appropriate thermodynamic data from Table 1 gives $\Delta G^\circ = -393.9$ kJ for the reaction as written above. The standard cell voltage can then be calculated from eq 2. The result is $E_{\text{cell}}^\circ = 2.04$ volts. These values reveal that the reaction is slightly more favored in the formalism of the rigorous model. This should be expected since the fully dissociated acid of this model is immediately available to form PbSO_4 and H_2O .

Activities must be assigned to all species in this model without approximations. The Pb , PbO_2 , and PbSO_4 activities can again be taken as 1 because these substances are in their standard states. The activity assigned to H_2O , on the other hand, must recognize that the water contains dissolved acid. In general, a solute lowers the activity of its solvent. The extent of lowering can be determined from the decrease in the solvent vapor pressure. When water is the solvent we have

$$a_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^\circ}$$

where $P_{\text{H}_2\text{O}}$ is the vapor pressure of water over the solution and $P_{\text{H}_2\text{O}}^\circ$ is the vapor pressure of pure water.² Using this method $a_{\text{H}_2\text{O}}$ has been determined (2) over a broad range of sulfuric acid concentrations (see Table 2). As shown in Figure 3 the activity is very nearly 1 in dilute solutions, but it drops when the concentration exceeds 1 molal.

The assignment of activities to H^+ and SO_4^{2-} must acknowledge that the behavior of these species is far from ideal. In general, deviations from ideality for a solute are accounted for by introducing an empirical correction factor γ called the *activity coefficient*. The activities of the two ions are then written

$$a_{\text{H}^+} = \frac{2\gamma_+ m}{m^\circ} \quad \text{and} \quad a_{\text{SO}_4^{2-}} = \frac{\gamma_- m}{m^\circ}$$

where γ_+ and γ_- are the activity coefficients for the respective ions, m is the H_2SO_4 molality, and m° is the standard concentration of 1 molal. It is not possible to measure the activity coefficients of individual ions because ions always exist in pairs, rather than alone. However, the *mean activity coefficient* γ_\pm of a pair of ions can be measured. It is defined as the geometric mean of the individual activity coefficients (3–5). This combined parameter will serve our purpose just as well. In

Table 2. Activity of H_2O and Mean Activity Coefficient of H_2SO_4 in Aqueous Sulfuric Acid (2)

H_2SO_4 Molality	$a_{\text{H}_2\text{O}}$	γ_\pm
0.001	0.999950	0.8045
0.003	0.999857	0.6962
0.010	0.999560	0.5420
0.030	0.998812	0.3902
0.1	0.996437	0.2508
0.3	0.98944	0.1700
1.0	0.96155	0.1247
3.0	0.85174	0.1337
10.0	0.36169	0.5270
20.0	0.08529	1.7015

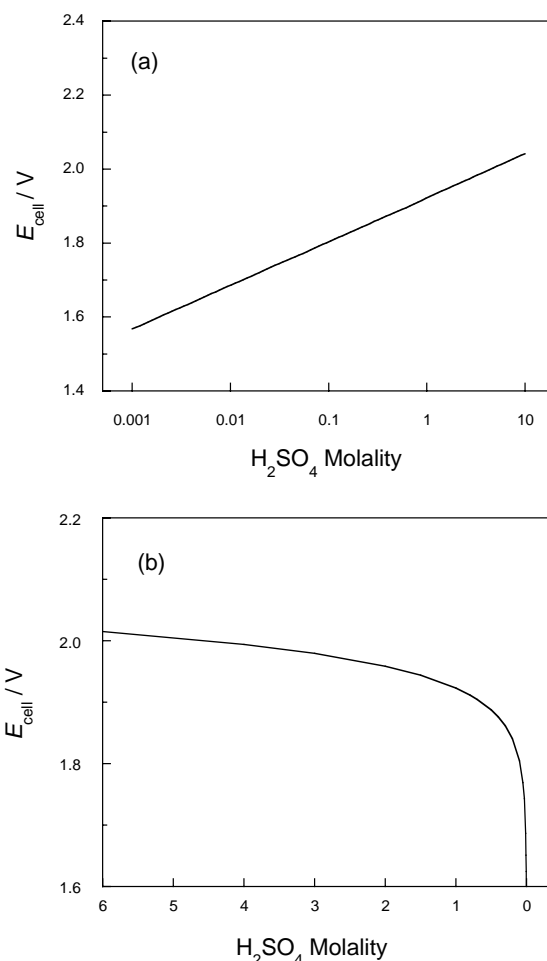


Figure 2. Lead-acid cell voltage versus acid concentration calculated from the approximate model.

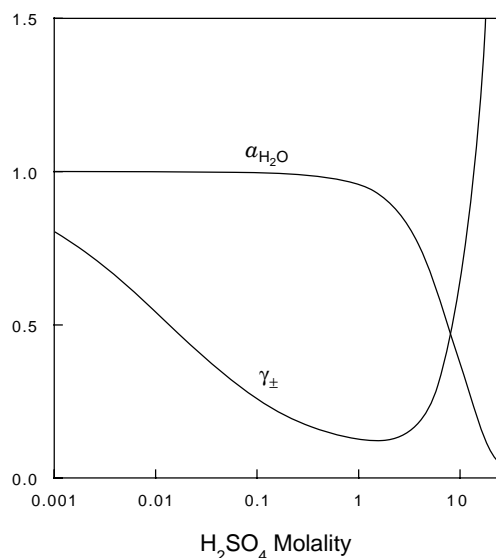


Figure 3. Plots of the activity of water and the mean activity coefficient of sulfuric acid versus H_2SO_4 molality.

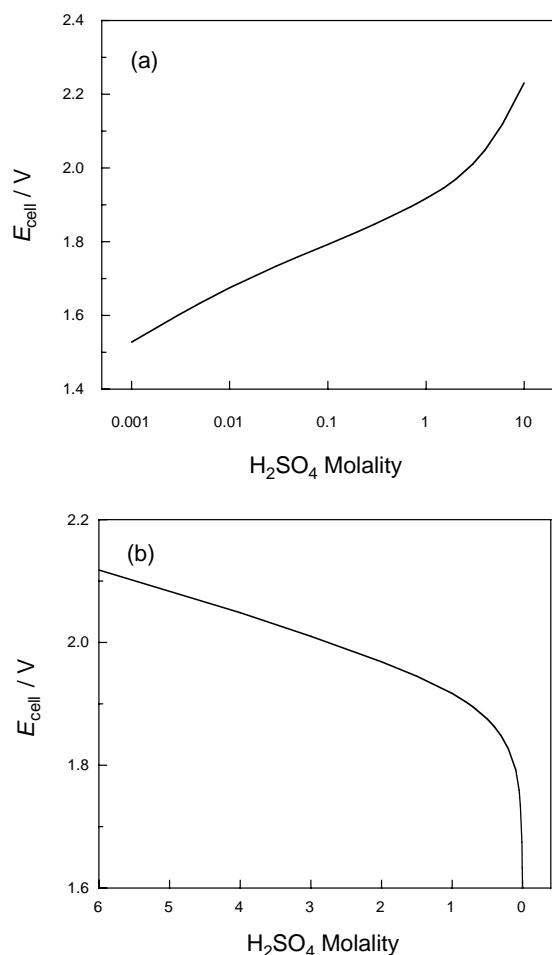


Figure 4. Lead-acid cell voltage versus acid concentration calculated from the rigorous model.

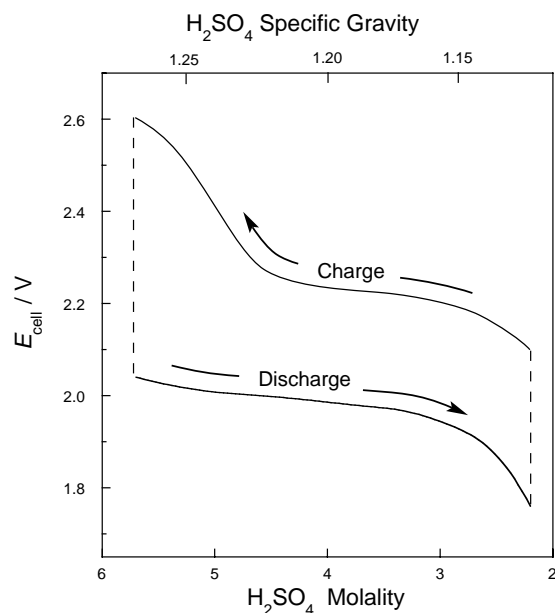


Figure 5. Voltage of an actual lead-acid cell during a discharge and charge cycle at constant current.

the case of a 2:1 electrolyte such as H_2SO_4 , it is

$$\gamma_{\pm} = (\gamma_+^2 \gamma_-)^{1/3}$$

The mean activity coefficient of H_2SO_4 in aqueous solution has been determined (2) over a range of concentrations from measurements of the electromotive force of galvanic cells that employ the acid as their electrolyte (see Table 2). Figure 3 plots γ_{\pm} versus H_2SO_4 molality. The coefficient equals 1 at infinite dilution because at that concentration the acid dissociates fully and its ions behave ideally. The value drops with concentration as nonideality sets in. It then increases at high concentration as the solution becomes deficient in water.

The reaction quotient for the rigorous model is

$$Q = \frac{(a_{\text{H}_2\text{O}})^2}{(a_{\text{H}^+})^4 (a_{\text{SO}_4^{2-}})^2}$$

which upon substitution of the expressions for the activities and the mean activity coefficient becomes

$$Q = \frac{(a_{\text{H}_2\text{O}})^2}{\left[4 \left(\frac{\gamma_{\pm} m}{m^{\circ}}\right)^3\right]^2}$$

Insertion of this expression into the Nernst equation allows calculation of the cell voltage at any acid concentration. For example, in 0.1 molal H_2SO_4 we have $a_{\text{H}_2\text{O}} = 0.996437$ and $\gamma_{\pm} = 0.2508$. These values give $E_{\text{cell}} = 1.79$ volts. This result agrees well with the voltage we calculated earlier for the same concentration using the approximate model. Figure 4 shows cell voltage versus acid concentration according to the rigorous model. The graphs are in the same style as those of Figure 2. The two models yield nearly identical results except at very low or high acid concentrations. At these conditions the rigorous model should be considered more valid.

In the theoretical models the cell under consideration is in a state of thermodynamic equilibrium in that no current is flowing through it. The voltages we have calculated are *open-circuit* voltages. In the next section we discuss a cell of a different type. It is a practical cell in the process of being charged or delivering electrical energy. It is not in a state of equilibrium.

Actual Battery Performance

The voltage a battery delivers when it is discharging or that it requires for charging is a matter of practical concern for electrochemical engineers (6–12). Figure 5 shows the performance of a typical lead-acid cell during a cycle in which it is discharged and recharged at constant current. Its voltage is plotted against the concentration and specific gravity of the electrolyte. As is typical of rechargeable batteries, the discharge voltage is consistently lower than the charging voltage. This behavior is attributable to several factors collectively known as *cell polarization*.

Three types of polarization occur in any electrochemical cell through which a current is flowing. *Activation polarization* results from the chemical processes occurring at the electrodes. These include bond breaking and formation, solvation changes,

formation of new phases, and the transport of reacting species through the electrode. Each process has an activation energy that must be constantly supplied if the cell is required to produce a current. *Concentration polarization* results from concentration gradients that develop in the electrolyte where it contacts the electrodes. These gradients cause the concentrations of reacting species at the electrodes to differ from those of the bulk electrolyte. These first two types of polarization cause a drop in the cell electromotive force attributable to a specific electrode. The drop is known as the electrode *overvoltage*, η . *Ohmic polarization*, on the other hand, occurs in the bulk of the electrolyte. It results from the resistance the electrolyte offers to the movement of ions through it. In keeping with Ohm's law, the voltage loss is IR , the product of current times resistance.

Each type of polarization causes a drop in the voltage delivered by a discharging cell. Thus

$$E_{\text{discharge}} = E_{\text{cell}} - \eta_{\text{cathode}} - \eta_{\text{anode}} - IR$$

where E_{cell} is the open-circuit voltage and the terms subtracted from it are the electrode overvoltages and ohmic loss. The voltage required to charge a cell, on the other hand, can be calculated by adding the three polarization terms. Electrode overvoltage and ohmic loss account for the fact that the charging and discharging curves of Figure 5 differ from one another and from the open-circuit curve of Figure 4b. The advanced literature can be consulted for further details (6–12).

Figure 6 is a cutaway view of an actual lead–acid battery. The components shown are the positive and negative plates, a layer of lead(IV) oxide, and a porous separator. Separators are thin sheets placed between the plates of a battery. They are permeable to the electrolyte but they prevent the plates from making direct contact and short-circuiting the cell.

Conclusions

The cell voltage calculated by the approximate model agrees well with that of the rigorous model when the acid concentration is in the 0.1 to 1 molal range. Apparently the assumptions of the model are acceptable in this concentration range. In more dilute solutions the model loses accuracy because the deprotonation of HSO_4^- is not considered.³ At concentrations greater than 1 molal its assumptions of ideality begin to falter. In spite of these limitations, the approximate model can serve as a learning experience for general chemistry students. It serves well to illustrate a practical application of the Nernst equation. Students can be challenged to create a plot of cell voltage versus extent of discharge. The rigorous model yields accurate open-circuit voltages at all concentrations. For physical chemistry students it provides experience in dealing with solvent and solute nonideality. However, it is also limited in that it gives only the voltage of a cell through which no current is flowing. A complete understanding of the practical lead–acid cell requires knowledge of such factors as electrode overvoltage and ohmic loss.

Notes

1. When performing calculations with the Nernst equation it is helpful to note that $RT/F = 0.025693$ volts at 298.15 K.
2. This equation is modified for highly accurate work to take into account the nonideality of water vapor.

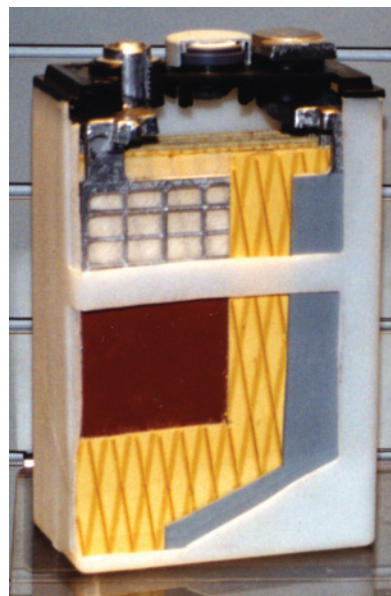


Figure 6. Cutaway view of an industrial lead–acid battery. Photo courtesy of Independent Battery Manufacturers Association, IBMA.

3. The approximate model can be improved at low concentrations by taking into account that in dilute solutions a substantial fraction of the HSO_4^- present is deprotonated. The H^+ and HSO_4^- concentrations used to evaluate Q can be corrected for that fact. However, the correction makes the model considerably more mathematically complex, and it has only a very small effect on the calculated value of E_{cell} .

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