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How Batteries Store and Release Energy: Explaining Basic Electrochemistry

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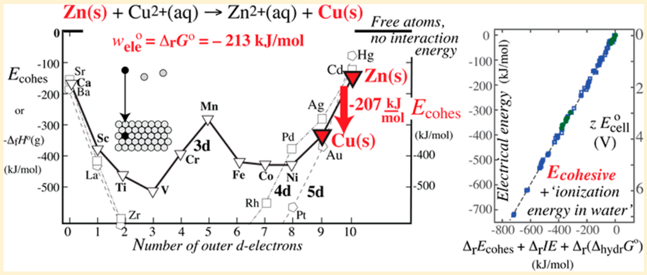
S *Supporting Information*



ABSTRACT: Batteries are valued as devices that store chemical energy and convert it into electrical energy. Unfortunately, the standard description of electrochemistry does not explain specifically where or how the energy is stored in a battery; explanations just in terms of electron transfer are easily shown to be at odds with experimental observations. Importantly, the Gibbs energy reduction in an electrochemical reaction in a battery also involves atom transfer between different phases. It is shown that, for simple galvanic cells or batteries with reactive metal electrodes, two intuitively meaningful contributions to the electrical energy are relevant: (i) the difference in the lattice cohesive energies of the bulk metals, reflecting metallic and covalent bonding and accounting for the atom transfer, and (ii) the difference in the ionization energies of the metals in water, associated with electron transfer. The ionization energy in water can be calculated as the sum of gas-phase ionization energies and the hydration energy of the metal ion. Entropy plays only a limited role, for instance, driving the processes in concentration cells. The prediction of the energy of batteries in terms of cohesive and aqueous ionization energies is in excellent agreement with experiment. Since the electrical energy released is equal to the reduction in Gibbs energy, which is the hallmark of a spontaneous process, the analysis also explains why specific electrochemical processes occur. In several important cases, including the classical Zn/Cu battery, the difference in the bulk-metal cohesive energies is the origin of the electrical energy released. For instance, metallic Zn, Cd, or Mg lack stabilization by bonding via unoccupied d-orbitals and are therefore of higher energy than most transition metals. Indeed, metallic zinc is shown to be the high-energy material in the alkaline household battery. The lead−acid car battery is recognized as an ingenious device that splits water into 2 $H^+(aq)$ and O^{2-} during charging and derives much of its electrical energy from the formation of the strong O−H bonds of H_2O during discharge. The analysis provides an explanation of basic electrochemistry that will help students better understand this important topic.

KEYWORDS: *First-Year Undergraduate/General, Upper-Division Undergraduate, Electrochemistry, Electrolytic/Galvanic Cells/Potentials, Misconceptions/Discrepant Events, Textbooks/Reference Books*

■ INTRODUCTION

The storage of energy in batteries continues to grow in importance, due to an ever increasing demand for power supplying portable electronic devices and for storage of intermittently produced renewable energy. Where or how this energy is stored in a battery or its component galvanic cells should be explained in terms of electrochemistry, but unfortunately, the descriptions given in most general chemistry,[1−4] physical chemistry,[5−8] or electrochemistry[9,10] textbooks do not address this fundamental question. Instead, the energy produced by a given electrochemical process is calculated on the basis of standard reduction potentials looked up in a table.[11] Since the values in the table are not explained convincingly in terms of more basic chemical principles, this approach lacks insight and leaves students wondering.[12−14]

A related question that should be answered in any discussion of batteries and electrochemistry is why specific electrochemical reactions occur as they do. As for other spontaneous processes, a reduction in (Gibbs) energy is characteristic of spontaneous electrochemical reactions; since this decrease in free energy, ΔG, is known to equal the electrical work (i.e., energy) given off by the battery or galvanic cell under optimum conditions,[6,7,15] the questions of spontaneity and energetics could be answered by the same Gibbs energy analysis. However, this line of analysis has rarely been pursued; instead, the unexplained spontaneous appearance of a voltage (or electromotive force, emf, to make the description even more mysterious) has been emphasized.[12,16] Sometimes, the emf has been attributed to the spontaneous formation of an electrical double layer at the electrode surface,[4,16] but without a meaningful explanation for why that process occurs differently for different metals. Why positively charged ions move to the positive electrode (see Figure 1a) has also not been explained.[12] Calculating ΔG from tabulated Gibbs free energies of formation, while producing accurate numerical answers, does not provide any insight into the origin of the electrical energy or

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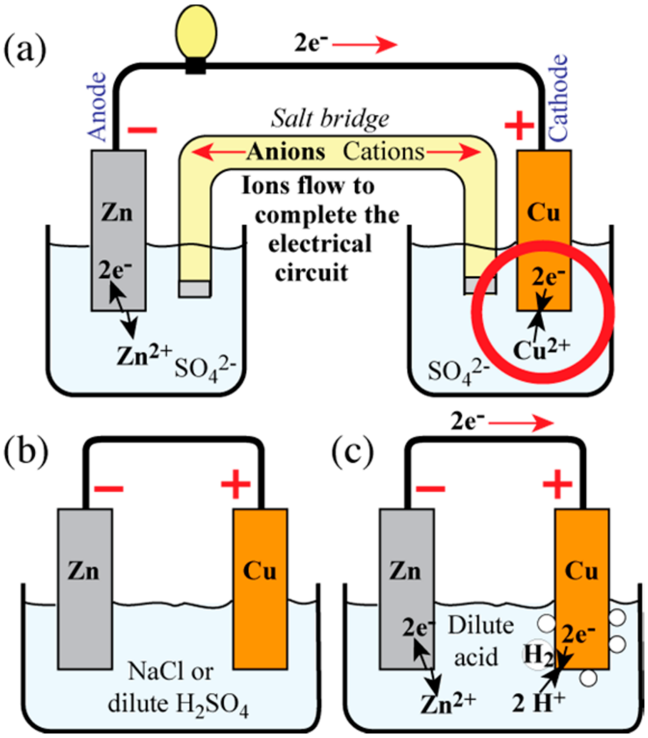

Figure 1. Galvanic cells. (a) Movement of ions and electrons in a Daniell cell, highlighting (red circle) that, at the cathode, positively charged ions move spontaneously to the positive lead of the battery. (b) Representation of a galvanic cell in some physics textbooks.[21−24] In this setup, which is equivalent to a potato or lemon battery[25] and to a cell in Volta's first battery, a voltage is produced independently of the nature of the more noble metal, due to (c) the reduction of hydrated H^+ ions (produced by an acid, including CO_2, or by autoprotolysis of H_2O) to $H_2(g)$ (bubbles shown as circles),[25] which occurs on the Cu electrode due to a kinetic barrier for this process on Zn.

electrochemical driving force, since the referencing of the Gibbs free energies of formation to H_2, O_2, Zn(s), Cu(s), etc. at 0 kJ/mol hides crucial bond[17,18] or bulk-metal cohesive energies;[19] for solvated ions, the referencing to $H^+(aq)$ is convenient but makes the tabulated values even more meaningless.[20] Some authors[21−24] even present the setup of a galvanic cell in a misleading way, altogether ignoring the need for ions of a relatively noble metal in solution and leaving out the separation between anode and cathode compartments (see Figure 1b). This leads to a more complicated electrochemical process occurring (see Figure 1c), which is usually not described.

With the basic driving force and energetics of batteries unexplained, it is no wonder that students (and many faculty) continue to struggle with the topic.[12−14] Teaching of electrochemistry in terms of long lists of facts and definitions that students should memorize[4,12−14] does not address this lack of fundamental conceptual understanding. The situation is also not improved by disagreements in the education literature about subtle questions such as whether[4,16] or not[12] the electrodes carry charge (they generally do,[9] which plays a role in driving the electrons through the external circuit, but as for macroscopic capacitors at low voltage, the magnitude of the stored charge is very small).

Scientists who study electrochemistry long enough memorize the order of the reactions in the table of standard reduction potentials[11] and on that basis develop an intuition about the relative tendency of metals or other species to be reduced; however, this approach is only tenuously connected to meaningful principles of chemistry. It still does not explain why, for instance, Cu and Zn, though being neighbors in the periodic table with similar properties of their ions, have greatly different standard reduction potentials.

Looking for understanding, many students, some professors,[8,26] and various secondary references[24,27,28] have constructed simplistic, usually incorrect explanations, often centered on the transfer of electrons emphasized in the teaching of redox reactions. For instance, it has been proposed that batteries work because metals (or metal ions) of different "affinities"[28] or maybe electronegativities[8,29] attract electrons differentially[27] or that "a voltaic cell operates because species in the two half-cells differ in their tendency to lose electrons."[26] These explanations are quickly disproved: The electronegativities of Cu and Ni are very similar, but their standard cell voltage is considerable, 0.57 V, corresponding to 110 kJ/mol of electrical energy; even more strikingly, in a concentration cell, the species in the two half cells (electrodes as well as ions in solution) are the same, yet a cell voltage is observed.

Rather than the difference in electronegativity (a quantity that is "erratic and largely unrealistic" for transition metals[30] and absent from the quantitative analysis of electrochemistry[9,10]), the difference in the total ionization energies of the two metals could be considered as a realistic measure of the relative binding energy of electrons, or of the resistance to releasing electrons. This predicts correctly that the easily ionized alkali metals are found near the bottom of the table of standard reduction potentials. However, it also leads to many incorrect predictions: ionization of Al(g) to $Al^{3+}(g)$ requires 7 times more energy than ionization of Ag(g) to $Ag^+(g)$, yet in an Al/Ag battery, $Al^{3+}(aq)$ is formed spontaneously as $Ag^+(aq)$ is reduced to Ag(s). For a Ni/Cd galvanic cell, the ionization-based explanation similarly predicts the direction of the electrochemical reaction incorrectly: ionization of Cd is unfavorable relative to Ni ionization (see Table 1), and the difference is even greater for the solvated ions, yet $Cd^{2+}(aq)$ is formed spontaneously as $Ni^{2+}(aq)$ is reduced. Furthermore, $Zn^{2+}(aq)$ is *less* favored than $Pt^{2+}(aq)$ by 45 kJ/mol, yet Zn(s) is much easier to oxidize to $Zn^{2+}(aq)$ than Pt(s) is to $Pt^{2+}(aq)$. This demonstrates that important aspects are missing from the electron-transfer or ionization-based analysis. A plot of the half-cell potential vs the total gas-phase ionization energy for various metals commonly involved in electrochemical reactions in Figure 2 exhibits no strong correlation between the two quantities, confirming that the tendency to release electrons does not by itself explain electrochemical processes.

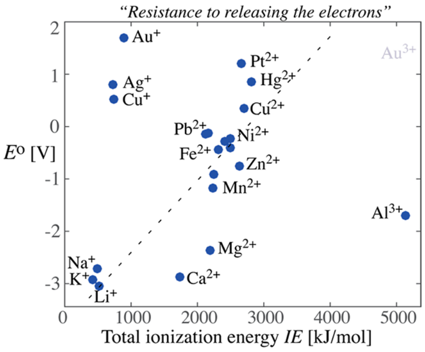

Figure 2. Standard reduction potential E° vs the total ionization energy IE (i.e., the energy needed to remove the z electrons) for various metal ions. No significant correlation is observed.

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Table 1. Meaningful Enthalpies and Free Energies Relevant for Batteries[a]

	relative to the free atoms				relative to the free atoms		
Species	$H°$(kJ/mol)	$G°$ (kJ/mol)	IE (kJ/mol)	Species	$H°$(kJ/mol)	$G°$(kJ/mol)	$\Delta_{hydr}H°$ (kJ/mol)
H_2(g)	−436 (bond)	−406.5		H^+(aq)	+162	+210	−1150
O_2(g)	−498 (bond)	−463.5		OH^-(aq)	−1076[b]	−1006[b]	
H_2O(l)	−971 (bonds + cond)	−875.5					
	Cohesive				IE + Hydration		
Li(s)	−158	−126.7	519	Li^+(aq)	−58	−7	−578
Fe(s)	−416	−370.7	2320	Fe^{2+}(aq)	+254	+368	−2068
Ni(s)	−430	−384.5	2490	Ni^{2+}(aq)	+276	+395	−2213
Cu(s)	−338	−298.6	2703	Cu^{2+}(aq)	+486	+592	−2217
Zn(s)	−131	−95.2	2639	Zn^{2+}(aq)	+475	+583	−2164
Cd(s)	−112	−77.2	2499	Cd^{2+}(aq)	+572	+670	−1927
Pt(s)	−565	−520.5	2661	Pt^{2+}(aq)	∼440	+538	∼-2220

[a] Bond energies of molecules, cohesive energies of metals, total ionization energies (IE) of metal atoms, hydration energies, ionization energies in water ("IE + hydration"), and electron affinities (EA) of an anion. The free atoms are the zero-point references for the quantities given (except for hydration energies). Table S1 provides additional data. [b] Bond energy - EA + hydration energy.

In this paper, a simple explanation of the energy of simple batteries or galvanic cells is given in terms of two conceptually meaningful contributions: cohesive[19] ("lattice") energies and ionization energies in water.[31] The ionization energy in water can in turn be considered as the sum of ionization and hydration (solvation) energies, which are strongly correlated and can therefore be combined into one quantity. The importance of the lattice cohesive energy is highlighted: it reflects that, rather than just involving transfer of electrons, electrochemical processes in batteries often require the transfer of metal *atoms* out of or into the bulk. The atomic- or molecular-level origin of the energy of specific batteries, including the Daniell cell, the 1.5 V alkaline battery, and the lead−acid cell used in 12 V car batteries, is explained quantitatively. A clearer picture of basic electrochemistry emerges from this energy analysis.

■ ANALYSIS

Electrical Energy and Gibbs Energy Reduction

As for all chemical reactions, the driving force for electrochemical processes without an applied voltage at constant T and P is a reduction in Gibbs free energy, G. The change in G, ΔG, is also equal to the maximum electrical energy (the maximum electrical work, in the terminology of thermodynamics)

$$\Delta G = w_{ele,max} \tag{1}$$

as is generally accepted. This is derived rigorously in the Supporting Information (SI), where it is also discussed why the change in *internal energy* does not equal $w_{ele,max}$. As an example, consider the reaction in the Daniell cell

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$
$$\Delta_r G° = -\ 213 \text{ kJ/mol} \tag{2}$$

On an elementary level, one can analyze this process in terms of energy conservation: Zn(s) + Cu^{2+}(aq) are of relatively high (free) energy, and their conversion to lower-energy Cu(s) + Zn^{2+}(aq) is accompanied by a release of about 200 kJ electrical energy per mole of Zn or Cu. Under standard conditions, or for Cu^{2+}(aq) and Zn^{2+}(aq) at equal concentrations and T = 298 K, the maximum molar electrical work is the standard molar Gibbs free energy of reaction

$$\overline{w}_{ele,max} = \Delta_r G° \tag{3}$$

see eq S8 in the SI. Fortunately, even if the concentrations differ by a couple of orders of magnitude, $\overline{w}_{\ ele,max}$ deviates from $\Delta_r G°$ by only a few tens of kJ/mol, which is neglected here. According to eq 3, the origin of the electrical energy provided by a battery can be elucidated through an analysis of $\Delta_r G°$. It will be shown that $\Delta_r G°$ is dominated by two free-energy terms, each with a simple intuitive interpretation.

Two Energy Differences Drive a Simple Battery

For the Zn/Cu electrochemical reaction (eq 2), the Gibbs free energy (change) of reaction is, as usual, the difference between the molar Gibbs free energies of products and reactants:

$$\begin{aligned}\Delta_r G°_{ZnCu} &= G°_{Cu(s)} + G°_{Zn^{2+}(aq)} - (G°_{Zn(s)} + G°_{Cu^{2+}(aq)})\\ &= (G°_{Cu(s)} - G°_{Zn(s)}) + (G°_{Zn^{2+}(aq)} - G°_{Cu^{2+}(aq)})\end{aligned} \tag{4}$$

The first term, $G°_{Cu(s)} - G°_{Zn(s)}$ = −203.4 kJ/mol (from Table 1), is the difference between the free energies of the metals relative to the free atoms without bonding, while the second, $G°_{Zn^{2+}(aq)} - G°_{Cu^{2+}(aq)}$ = −9 kJ/mol, also from Table 1, is the difference in the ionization free energies of the two metals in water, discussed in more detail below. This analysis can be visualized as shown in Figure 3a, taking the molar free energies of free atoms as the zero point. Since the bulk-metal Gibbs energy difference is much larger than the ionization term, it is immediately clear that the electrical energy of a Zn/Cu battery is derived from the difference in the free energy of the two bulk metals. In the following, indeed, Zn(s) is found to be a high-energy metal, due to its net-zero d-electron bonding. Note that a crucial step in finding this simple explanation of the energetics of batteries is not to start by analyzing half reactions, where one has to compare a bulk metal with its ion and wonder about the energy of electrons.[9] In the full reaction, one can just compare bulk metal with bulk metal and solvated ion with solvated ion in terms of their free energies, see eq 4.

Entropic effects make only a minor (<3%) contribution to $\Delta_r G°_{ZnCu}$, since the entropies of the ions on both sides of the reaction (eq 1) are similar so at T = 298 K both factors in $-T\Delta_r S°_{ZnCu}$ are fairly small. Therefore, the analysis can be simplified by focusing on enthalpies, which have more immediate interpretations in terms of interactions. Again, taking the free atoms as the reference point, it becomes apparent that $H°_{Cu(s)}$ is the energy released when the atoms come together to

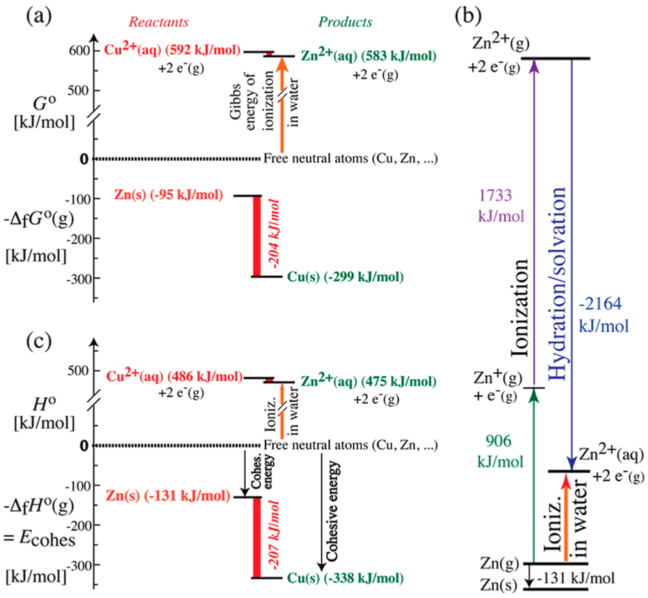

Figure 3. (a) Molar free energies G° of (bottom half) zinc and copper metals, and (top half) hydrated Cu^{2+} and Zn^{2+} ions, with reactants shown on the left and products on the right, where $G^\circ = H^\circ - TS^\circ$, with G°, H°, and S° relative to the free atoms. (b) The "ionization energy in water" can be calculated as the sum of the total gas-phase ionization energy IE (always positive) plus the hydration energy $\Delta_{hydr}H^\circ$ of the ion (always negative), as shown here for Zn^{2+}. The diagram for Cu^{2+} is shown in Figure S1. (c) Same as part a in terms of enthalpies, simplifying the analysis. The red vertical bars highlight that the electrical energy of the Zn/Cu cell derives mostly from the higher energy of zinc vs copper metal.

form bulk copper, i.e., the lattice cohesive energy[19] discussed in more detail below and in the SI

$$H^\circ_{\mathrm{Cu(s)}} = E_{\mathrm{cohes,Cu}} \tag{5}$$

Thus, the first term in eq 4 can be approximated as

$$\begin{aligned} G^\circ_{\mathrm{Cu(s)}} - G^\circ_{\mathrm{Zn(s)}} &\approx H^\circ_{\mathrm{Cu(s)}} - H^\circ_{\mathrm{Zn(s)}} \\ &= E_{\mathrm{cohes,Cu}} - E_{\mathrm{cohes,Zn}} = \Delta_r E_{\mathrm{cohes}} \end{aligned} \tag{6}$$

Analyzing the ionic term in eq 4, $G^\circ_{\mathrm{Zn^{2+}(aq)}}$, the ionization energy of Zn atoms in water, can be considered as the sum of two more familiar quantities: the energy $\mathrm{IE_{Zn}}$ of gas-phase ionization to Zn^{2+}(g) and the free energy of solvation/hydration of Zn^{2+}(g). See Figure 3b and the discussion below. Thus

$$\begin{aligned} & G^\circ_{\mathrm{Zn^{2+}(aq)}} - G^\circ_{\mathrm{Cu^{2+}(aq)}} \\ &\approx \mathrm{IE_{Zn}} + \Delta_{\mathrm{hydr}} G^\circ_{\mathrm{Zn^{2+}}} - (\mathrm{IE_{Cu}} + \Delta_{\mathrm{hydr}} G^\circ_{\mathrm{Cu^{2+}}}) \\ &= \Delta_r(\mathrm{IE} + \Delta_{\mathrm{hydr}} G^\circ) \end{aligned} \tag{7}$$

with $\Delta_r\mathrm{IE} = \mathrm{IE_{Zn}} - \mathrm{IE_{Cu}}$, and one can rewrite the electrical energy of the Zn/Cu battery in terms of the differences in cohesive, ionization, and hydration energies:

$$\Delta_r G^\circ_{\mathrm{ZnCu}} \approx \Delta_r E_{\mathrm{cohes}} + \Delta_r(\mathrm{IE} + \Delta_{\mathrm{hydr}} G^\circ) \tag{8a}$$

$$\approx \Delta_r E_{\mathrm{cohes}} + \Delta_r(\mathrm{IE} + \Delta_{\mathrm{hydr}} H^\circ) \tag{8b}$$

$$= -207\ \mathrm{kJ/mol} - 11\ \mathrm{kJ/mol} \tag{8c}$$

The result is within a few percent from the experimental value of −213 kJ/mol. Figure 3c shows the relevant enthalpy differences and again highlights that the electrical energy of a Zn/Cu battery mainly derives from the difference in the cohesive energies of the bulk metals.

Metal Lattice Energy and d-Electron Bonding

The lattice cohesive energies of the bulk metals play a crucial role in eqs 5, 6, and 8a. E_{cohes} is the energy of metallic and covalent bonding in the bulk metal and is released when free metal atoms come together and form the solid (or liquid) metal. It is conceptually quite analogous to the lattice energy of an ionic solid, which is familiar to chemists. Therefore, we include the term "lattice" with cohesive energy. Further conceptual aspects of the lattice cohesive energy are discussed in the SI.

Apart from its sign, the lattice cohesive energy is the same as the energy required to atomize a metal at ambient conditions. It therefore has the same magnitude as the enthalpy of sublimation, $\Delta_{\mathrm{subl}}H$, or the standard enthalpy of formation of the metal gas, $\Delta_f H^\circ(g)$, since the solid metal is the standard state of the element. The values of $\Delta_f H^\circ(g)$ are tabulated for many metals in General Chemistry textbooks.[32] Table 1 and Table S1 list the lattice cohesive energies for various metals of interest in electrochemistry.

The lattice cohesive energy varies across the series of transition metals in a systematic way.[31] As Figure 4 shows, it increases with the number of partially filled d-orbitals, indicating their strong contribution to bonding in transition metals. As the d-shell fills up, the successive filling of antibonding orbitals or energy bands cancels the bonding effect. For instance, Zn has no net d-electron bonding, which is reflected in its low melting point and small magnitude of lattice cohesive energy, while Cu(s) is stabilized by bonding via one net d-orbital. Relative to most transition metals, the group 1, 2A, and 2B metals (e.g. Li, Na, K, Rb, Cs, Mg, Ca, Zn, Cd, and Hg) stand out in terms of weakly negative (i.e., high) cohesive energies (magnitude < 180 kJ/mol). This is a major reason that most of these metals easily undergo oxidation, e.g., $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$, which requires atom transfer out of the metal against the bonding forces associated with the cohesive energy. Therefore, these metals appear low in the table of standard reduction potentials and are commonly used as anodes in batteries. (Hg does not follow this prediction since its unusually weak cohesion is significantly compensated by an unusually high ionization energy in water.)

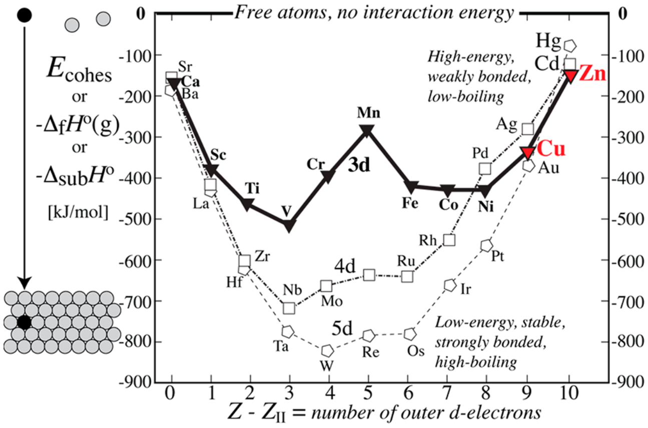

Figure 4. Dependence of the molar lattice cohesive energy E_{cohes} $(= -\Delta_f H^\circ(g) = -\Delta_{\mathrm{subl}} H^\circ)$ of transition metals. Stable, low-energy metals are shown with low energy. The 200 kJ/mol difference between Cu and Zn metals due to increased d-electron antibonding in Zn is clearly visible.

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Importance of the Lattice Cohesive Energy for Batteries

The $Cd(s)|Cd^{2+}(aq)||Ni^{2+}(aq)|Ni(s)$ cell provides a particularly clear example of the importance of the lattice cohesive energy: In the reaction

$$Cd(s) + Ni^{2+}(aq) \rightarrow Cd^{2+}(aq) + Ni(s)$$

$$\Delta_r G^\circ = -33 \text{ kJ/mol} \tag{9}$$

metallic Cd spontaneously converts to $Cd^{2+}(aq)$, while $Ni^{2+}(aq)$ is reduced to metallic Ni. One might be tempted to conclude that this reaction is spontaneous because Cd is easier to ionize than Ni, but this is incorrect. Cd is in fact more *difficult* to ionize than Ni, since the first ionization energy of Cd is higher by about 130 kJ/mol,[31] and the combined first and second ionization energy still by 9 kJ/mol (see Table 1). Furthermore, hydration of Cd^{2+} is *less* favorable than that of Ni^{2+}, by 266 kJ/mol (see Table 1), precluding an explanation in terms of more favorable interactions of Cd^{2+} with water. The driving force for this reaction is the large (−317 kJ/mol) difference in the lattice cohesive energies of the metals, see Figure 3 and Table 1.

In the Zn/Cu battery, eq 2, the metal cohesive energy is also the main (>75%) source of the electrical energy. At −206 kJ/mol, it is 3 times larger than the difference in ionization energies, −64 kJ/mol,[31] and that difference is mostly canceled by the Gibbs energy of hydration of Zn^{2+}, which is actually *unfavorable* relative to Cu^{2+}, by +52 kJ/mol (Table 1). As a result, the ionization energies of Zn and Cu in water end up being very similar. Interestingly, Zn^{2+} and Pt^{2+} have comparable ionization and hydration energies, and $Zn^{2+}(aq)$ is *less* favored than $Pt^{2+}(aq)$ by 45 kJ/mol (Table 1), so the energy released ($\Delta_r G^\circ$ = −380 kJ/mol) in the spontaneous reaction

$$Zn(s) + Pt^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pt(s) \tag{10}$$

is due to the metals' correspondingly different lattice cohesive energies, see again Figure 3.

As will be shown below, ions are only intermediates, not reactants or products, in alkaline or lithium batteries. This means that ionization energies are not particularly important in those systems, while cohesive energies play a role in most batteries. Cohesive energies of metals or oxides are analogous to bond energies of molecules, which are directly relevant when molecules are involved in electrochemical reactions (see examples below).

Ionization and Hydration Energies

In addition to the cohesive energies emphasized so far, gas-phase ionization and hydration energies also contribute to the energy given off by a simple battery if ions are reactants or products, see eq 8a. Gas-phase ionization energies reflect the outer electronic shell structure of an atom and are discussed in most General Chemistry texts. The quantity of interest here is the *total* ionization energy IE, which for an ion of charge number $+z$ is the sum of the ionization energies up to the zth value. Total ionization energies relevant in electrochemistry range between 418 kJ/mol for $K^+(g)$ and >5 MJ/mol for $Al^{3+}(g)$.

The hydration or solvation energy of an ion is released when the ion is placed into water. Its magnitude ranges from ∼300 kJ/mol for $Cs^+(g)$ to >4 MJ/mol for $Al^{3+}(g)$. Its trends are easy to explain semiquantitatively: The magnitude of the hydration energy increases with the square of the charge of the ion and inversely to its radius.[31] Hydration enthalpies and entropies are conventionally given relative to $H^+(aq)$, which obscures the strength of the ion−solvent interaction.[20] While the absolute values of hydration enthalpies and free energies are known only with uncertainties of a few tens of kJ/mol,[20,33,34] this does not significantly change the trends observed. Furthermore, any calculated results are as accurate as those obtained with the (meaningless) conventional values, since errors from this source exactly cancel. We have used the widely accepted absolute H^+ hydration enthalpy of −1150 kJ/mol and free energy of −1105 kJ/mol proposed by Tissandier et al.[33]

The lowest gas-phase and aqueous ionization energies are observed for the alkali metals, see Figure 5, and in combination with their moderate cohesive energies account for their easy oxidation. This relation between the alkalis' small gas-phase ionization energies and low position in the table of standard reduction potentials has long been known, but the analysis was still very incomplete, for instance missing contributions of the hydration and cohesive energies. Therefore, it does not generalize, see Figure 2, and has only very limited explanatory power.

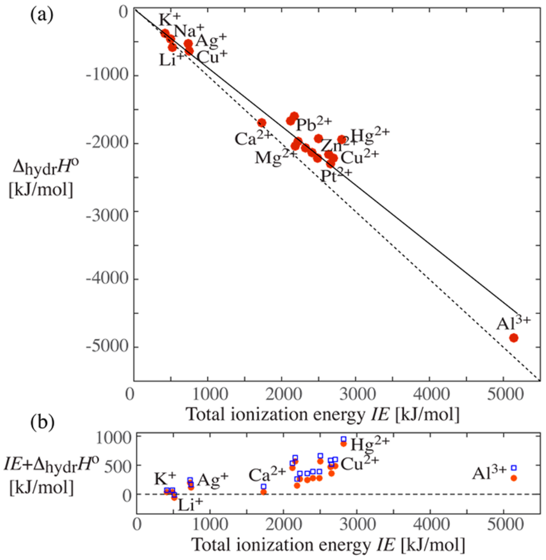

Figure 5. (a) Plot of the hydration enthalpy of 19 metal ions as a function of the total gas-phase ionization energy needed to generate the ion. The sum of the two quantities (which have opposite signs) is the ionization energy in water, plotted in part b (red ●); the ionization *free* energy in water is also shown (blue ☐).

Ionization Energy in Water

The ionization energy in water is a conceptually meaningful quantity, namely, the difference between the energy of the ion in water plus the electron in the gas phase, relative to the energy of the free (i.e., gas-phase) atom. Thus, it is conceptually analogous to the gas-phase ionization energy, but for an ion that goes into solution. It is the sum of the gas-phase ionization energy and the hydration energy, i.e., the difference of their magnitudes, see Figure 3b.

The magnitudes of the ionization and hydration energies are strongly correlated, see Figure 5a, in part because ionizing to a high charge requires a lot of energy and hydration of a highly charged ion releases a lot of energy. As a result, their sum, the ionization energy in water, is smaller in magnitude than either energy in the sum, rarely exceeding 700 kJ/mol (see Figure 5b). Ionization enthalpies and free energies in water of various ions of interest in electrochemistry are listed in Table 1 and Table S1.

Unlike the difference in cohesive or ionization free energies, the hydration free energy difference often has a significant

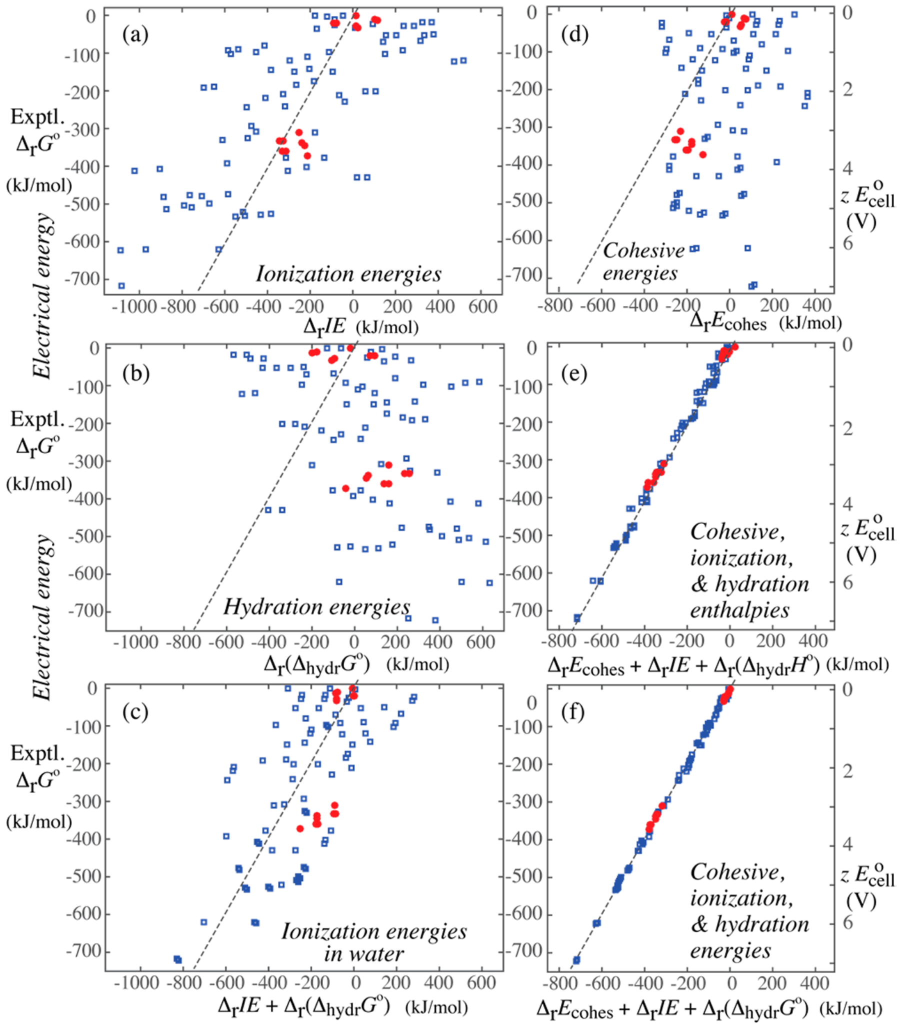

Figure 6. Values of $\Delta_r G^\circ = zFE^\circ_{cell}$, the experimental electrical energy available from simple metal-based batteries (galvanic cells) under standard conditions and per mole, for 93 pairs of 19 metals of equal charge number $z = 1$ or 2, plotted as a function of the difference in (a) the metal ionization energies; (b) the metal ion solvation/hydration free energies; (c) the sum of the metal ionization and hydration free energies; (d) the lattice cohesive energies; (e) the sums of the cohesive, ionization, and hydration enthalpies; and (f) the sums of the cohesive energies, ionization energies, and hydration free energies. Red ●: ion charges of $z = 1$. Blue □: ion charges of $z = 2$. The corresponding cell voltages, multiplied by the charge number z, are shown on the right vertical scale.

entropic contribution,[20] reflecting differences in ordering of the water molecules around different ions. Since the hydration enthalpy is not particularly familiar in General Chemistry, one can consider the full hydration free energy in its place, and calculate the energy, per mole, of a galvanic cell or battery under standard conditions to a good approximation as

$$\Delta_r G^\circ_{ZnCu} \approx \Delta_r E_{cohes} + \Delta_r(\mathrm{IE} + \Delta_{hydr} G^\circ) \qquad (11)$$

Generalized Quantitative Analysis of the Energetics of Galvanic Cells

The analysis for Zn/Cu and the result, eq 11, can be applied to any pair of metals with the same charge number of the ions. Figure 6a,b shows plots of $\Delta_r G^\circ$, the electrical energy given off by a battery (under standard condition per mole of reaction), as a function of the gas-phase ionization energy difference or the hydration energy difference; the data scatter widely. Plotted as a function of the sum of these differences, i.e., the difference in the ionization energies in water, $\Delta_r G^\circ$ shows a moderate correlation, see Figure 6c, complementary to that in the plot vs the lattice energy difference in Figure 6d. However, the plot according to eq 8a (with three enthalpy differences) shows a good correlation, and that according to eq 11 (with the difference in the free energy of hydration) shows an excellent correlation, see Figure 6e,f, respectively. This proves that the fairly simple analysis according to eq 11 has taken into account the crucial energy terms. The analysis for reactions involving differently charged ions (e.g., $Zn^{2+}(aq)$ and $Ag^+(aq)$) is more complex, with stoichiometric weighting and an explicit entropic term, and will therefore be deferred to a future publication.

Electron and Atom Transfer in Electrochemistry

Conventionally, electron transfer has been emphasized as a central aspect, and often as the driving force, of electrochemical processes.[24,27,28] However, it is only one out of three processes occurring in galvanic cells or simple batteries, specifically, (i) atom transfer out of the bulk metal into solution or into an oxide, or sometimes atom transfer out of a molecule like H_2O, see below; (ii) electron transfer from the atom to the bulk metal, leaving behind an ion (and from metal to cation at the other electrode); and (iii) hydration of the ion by the solvent molecules. The corresponding energies are (i) the lattice cohesive energies of the metals/oxides or the bond energies of molecules, (ii) the ionization energies of the atoms, and (iii) the hydration energies of the ions, which have all been discussed above and are visualized in Figure 3b.

It has been shown that the energy of the atom transfer sometimes dominates; in those cases, e.g., in the Zn/Cu Daniell cell, electron transfer should be considered as the consequence rather than the cause of the electrochemical process. In galvanic cells with a single ionic species, e.g., Li^+ in lithium batteries, the ion is necessarily an intermediate, and the energetic effects of electron transfer are subtle at best. Only a reaction limited to dissolved species without changes in covalent bonding, like $Cu^+(aq) + Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$, indeed involves just electron transfer and rearrangement of the solvent shells, without atom transfer. We have also documented that the magnitudes of the ionization (i.e., electron-transfer) energy (ii) and hydration energy (iii) are strongly correlated, see Figure 5, and their opposite signs make them mostly cancel.

Since the time of Volta, electron transfer in electrochemical reactions has sometimes[22,24] been confused with direct electron transfer between bulk metals due to differences in their true Fermi energies[35] or work functions.[36] Such a direct electron transfer is a fairly unrelated phenomenon that is very difficult to analyze since the true Fermi energy[35] or the work function of a metal immersed in water is hard to measure.[36] It can fortunately be ignored if electrons are not net reactants or products; this is the case when the *overall* reaction is considered, which is the approach chosen in this paper.

Everyday Batteries

The following three sections analyze the electrochemistry of everyday batteries and determine how these devices store energy. Readers specifically interested in basic electrochemistry can skip ahead to the section on Impact on Teaching, which describes how the energy analysis of galvanic cells developed here can be integrated into a General Chemistry course.

The 1.5 V Alkaline Battery

Analyzing the energetics of the overall cell reaction can also provide insights into how commercial batteries work and where their energy is stored. The most widely used household battery is the 1.5 V alkaline battery with zinc and manganese dioxide as the reactants. Six 1.5 V cells are also combined in series to produce a 9 V battery. The name "alkaline" derives from the hydroxide ion that plays a significant role as an intermediate in the half reactions of this battery. However, for understanding where the energy of this battery is stored, one only needs to analyze the relatively simple overall reaction[37] and the Gibbs free energies (cohesive free energies) of the metal and oxides involved (shown below the reaction; see the SI for the calculation of the values):

$$\mathbf{Zn(s)} + 2\,MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s) \qquad E^o_{cell} = 1.45\ V \qquad (12a)$$

G^o values: - 95 kJ/mol 2(-1102) -645 -1933 kJ/mol Δ_rG^o = -279 kJ/mol (12b)

Per atom: **-95 kJ/mol** -367 kJ/mol -322 -387 kJ/mol (12c)

Zn is seen to have a far higher free energy per atom than the oxides (−95 vs approximately −370 kJ/mol on average for the oxides). Thus, we can conclude that the energy of this battery is stored in Zn(s). This supports our previous conclusion that zinc is a high-energy metal. An alternative reaction often written for this battery, with H_2O added on the left-hand side and $Zn(OH)_2(s)$ instead of ZnO(s) shown as a product, gives the same $\Delta_rG°$ and cell voltage, as shown in the SI.

Li-Based Batteries

Modern batteries with high-energy density usually rely on Li^+ ions. These batteries require nonaqueous electrolytes since lithium metal reacts spontaneously with water, due to its weak metallic bonding, favorable formation of $Li^+(aq)$ (unlike many other cations, see Table 1 and Table S1), favorable bond formation in H_2, and highly favorable formation of solvated OH^- (values from Table 1):

$$Li(s) + H_2O(l) \rightleftharpoons Li^+(aq) + \tfrac{1}{2}\,H_2(g) + OH^-(aq) \qquad (13a)$$

$$\Delta_rG^o = \quad -(-127\ -876) \qquad -7 \quad + \tfrac{1}{2}(-407) \quad -1006 \quad = \ -214\ \text{kJ/mol} \qquad (13b)$$

The free-energy analysis of a Li-based battery is simple in some respects since only one ionic species ($Li^+(solv)$) is involved and it is only an intermediate that does not appear in the overall reaction or in $\Delta_rG°$. For instance, the net reaction in the lithium ion battery is

$$LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2 \qquad (14)$$

without any ionic species. We briefly focus on the conceptually simpler lithium−air battery, with an overall reaction of

$$2\,Li(s) \ + O_2(g) \rightarrow \quad Li_2O_2(s) \qquad E^o_{cell} = 2.96\ V\ (\text{ref. }^{38}) \qquad (15a)$$

G^o values: 2(-126.7) -463.5 kJ/mol -1288 kJ/mol Δ_rG^o = -571 kJ/mol (15b)

Per atom: **-127** kJ/mol -232 kJ/mol -321 kJ/mol (15c)

and meaningful cohesive and bond free energies from Table 1 and the Gibbs free energy of formation of $Li_2O_2(s)$ (which is $\Delta_rG°$).[38] The strong reduction in Gibbs free energy, $\Delta_rG° = -2 \times 96{,}485\ C/mol \times 2.96\ V = -571\ kJ/mol$, can be attributed to the relatively high energy per atom of Li metal (eq 15c) and the weak double bond of $O_2(g)$.[17,18] Electron transfer is only a minor aspect of the energetics of this process.

Water Splitting and Bond Formation in the Lead−Acid Battery

This secondary (i.e., rechargeable) battery is widely used in cars to power the ignition and a large number of electrical devices. It is commonly known as the 12 V battery since it usually contains six 2 V cells in series. While the energy of other batteries is stored in high-energy metals like Zn or Li as shown above, the energy of the lead−acid battery comes not from lead but from the acid. The energy analysis outlined below reveals that this rechargeable battery is an ingenious device for water splitting (into 2 H^+ and O^{2-}) during charging. Much of the energy of the battery is stored as "split H_2O" in 4 $H^+(aq)$, the acid in the battery's name, and the O^{2-} ions of $PbO_2(s)$; when 2 $H^+(aq)$ and O^{2-} react to form the strong bonds in H_2O, the bond free energy (−876 kJ/mol) is the crucial contribution that results in the net release of electrical energy.

The discharge process analyzed in the following is the reaction of lead metal as the anode and conductive lead dioxide, $PbO_2(s)$, on the cathode, with protons (in 38 wt %/wt aqueous H_2SO_4 when charged) to form $PbSO_4(s)$ and water:

$$Pb(s) + Pb\mathbf{O_2}(s) + \mathbf{4H^+(aq)} + 2SO_4{}^{2-}(aq) \rightarrow 2PbSO_4(s) + \mathbf{2H_2O} \qquad (16a)$$

$$\text{with } \nu_e = 2\ \text{electrons} \qquad \Delta_rG° = -396\ \text{kJ/mol}, \quad E°_{\mathbf{cell}} = 2.05\ V \qquad (16b)$$

The atoms that form H_2O are highlighted in bold. One can break this reaction down into two simpler steps to be added.

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In the first step, two combined half reactions produce 2 Pb^{2+}(aq), while in the second step, $2Pb^{2+}$(aq) precipitate with $2SO_4^{2-}$(aq) to form $2PbSO_4$(s):

$$\text{(i)}\quad \text{Pb(s)} \;+\; \text{Pb}\mathbf{O_2}\text{(s)} \;+\; \mathbf{4\,H}^+\text{(aq)} \rightarrow 2\,\text{Pb}^{2+}\text{(aq)} \;+\; \mathbf{2\,H_2O}(l) \qquad (17a)$$

$$-162\text{ kJ/mol}\quad -843\text{ kJ/mol}\quad +4\times 210\quad 2\times 639\text{ kJ/mol}\quad 2(-875.5\text{ kJ/mol}) \qquad (17b)$$

$$\text{(ii)}\;\; \mathbf{2}\,\text{Pb}^{2+}\text{(aq)} + \mathbf{2}\,\text{SO}_4^{2-}\text{(aq)} \rightarrow \mathbf{2}\,\text{PbSO}_4\text{(s)} \qquad \Delta_{sp}G^{o} = \mathbf{2} \times (-44\text{ kJ/mol})\text{ (see the SI)} \qquad (18)$$

Free energy values of the species involved in step i, relative to the free atoms, taken from Table S1 are shown below reaction i (eq 17). The lattice cohesive free energy of PbO_2 (−843 kJ/mol) was calculated from its enthalpy and entropy of formation as shown in the SI. The energy released when the bonds of H_2O are formed makes this reaction highly exergonic, while the formation of Pb^{2+}(aq) looks very unfavorable. Overall, step i produces a net $\Delta_rG° = -308$ kJ/mol. After adding −88 kJ/mol from the precipitation (ii) one obtains

$$\Delta_rG° = -308\text{ kJ/mol} - 88\text{ kJ/mol} = -396\text{ kJ/mol} \qquad (19)$$

$$E°_{\text{cell}} = -396\text{ kJ/mol}/(-2 \times 96{,}485\text{ C/mol}) = 2.05\text{ V} \qquad (20)$$

Concentration Cells

In a concentration cell, see Figure 7, both half-cells have the same electrode metals and ions, but the cation concentrations are different, e.g., Cu(s)|Cu^{2+} (0.1 M)|Cu^{2+} (0.3 M)|Cu(s). Concentration cells are conceptually important to immediately disprove any claims that batteries produce a voltage due to a different "electron affinity" of different metals.[8,26−29] The (initial) voltage of a concentration cell with 0.1 M and 0.3 M solutions is easily calculated by the Nernst equation with $E°_{\text{cell}} = 0$:

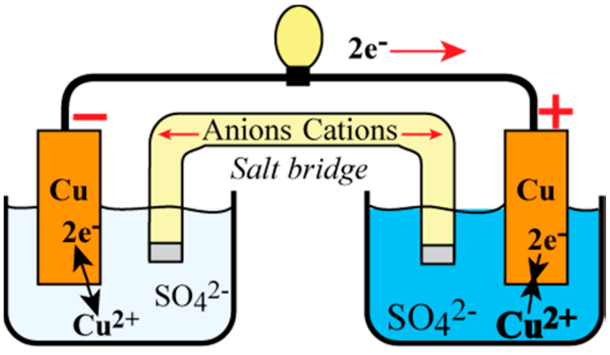

Figure 7. Schematic of a copper-based concentration cell. The equilibration of the Cu^{2+} concentrations is spontaneous, and the associated reduction in the total Gibbs free energy drives the cell processes. The electrical work is supplied as heat from the surroundings.

$$E_{\text{cell}} = -RT/(\nu_eF)\,\ln([\text{Cu}^{2+}]_{\text{low}}/[\text{Cu}^{2+}]_{\text{high}}) = 0.014\text{ V} \qquad (21)$$

As in all galvanic cells, the process is driven by a reduction in Gibbs free energy, $\Delta_rG < 0$, as concentrations equilibrate. It is obvious that concentration equilibration is a spontaneous process, but one can check that there really is a reduction in G, see the SI. The equilibration of concentrations is an *entropic* effect (as long as activities can be approximated by molarities divided by mol/L) because the overall amounts of ions and of metallic copper remain unchanged.

While this analysis explains why a concentration cell produces a voltage and current, it does not explain where its energy comes from. The analysis in the SI shows that $w_{\text{ele}} = -q$ when $\Delta_rH = 0$ for a galvanic cell (see eqs S2 and S3). In other words, a concentration cell converts heat from the surroundings into electrical work.

■ IMPACT ON TEACHING

The approach described in this paper provides relatively simple answers to the questions of why and how batteries give off energy, and thus fills a crucial conceptual gap right at the start of textbook descriptions of electrochemistry. The analysis presented above can be simplified as follows: Some metals have weaker bonding than others and are therefore of relatively high energy. Similarly, different metal ions in water have different energies because of their various interactions with electrons and water molecules. A galvanic (e.g., Zn/Cu) cell gives off electrical energy because a higher-energy metal dissolves while a lower-energy metal precipitates, and/or a higher-energy ion disappears as a lower-energy ion is generated. For the Zn/Cu cell, the electrical energy is essentially the difference between the bonding energies of zinc and copper. This leads to the concept of energy storage in metals such as Zn, Li, or Cd, which are less stabilized by bonding because they lack partially occupied d-orbitals. The author has used this approach twice in his General Chemistry course (see lecture notes at the end of the SI), with positive feedback from students.

By writing overall reactions, rather than starting with half reactions, the problem is greatly simplified: one can compare the energies of two bulk metals, and of two metal ions, without the complexities of electron energetics.[9,35,36] Half reactions still arise naturally when one goes on to explain how the electrochemical reaction will occur under the constraints imposed by the separation of the reaction system into half-cells (see Figure 1a): In order for the Zn/Cu reaction (eq 2) to occur, Zn(s) must convert to Zn^{2+}(aq), Zn(s) → Zn^{2+}(aq) + $2e^-$, which forces Zn to leave behind $\nu_e = 2$ electrons in the zinc electrode. At the same time, Cu^{2+}(aq) must be reduced to Cu(s), Cu^{2+}(aq) + $2e^-$ → Cu(s), which requires each copper ion to take up two electrons from the electrode. The electron excess in the zinc and the electron deficiency in the copper electrode drive electron flow through the external circuit, from zinc (too many electrons, hence the negative electrode) to copper (with an electron deficit, hence the positive lead of the battery). This is shown in Figure 1a and explains naturally why positive ions move to the positive electrode. Ion movement in the salt bridge completes the electric circuit.

Once this conceptual understanding has been established, one can remind students that oxidation is loss ("OIL") and reduction is gain ("RIG") of electrons and introduce the definitions of anode and cathode with useful mnemonics (ANode with OXidation, REDuction at the CAThode). For instance, Zn(s) → Zn^{2+}(aq) + $2e^-$ shows electron loss, oxidation, making the zinc electrode the anode. Next, the table of standard reduction potentials $E°$ can be used in the conventional way, after pointing out that it conveniently summarizes the cohesive energy and ionization energy in water of a given metal. The link between $E°$ and the free energy change is $E° = -\Delta_rG°/(\nu_eF)$, see the SI. The standard cell voltage can be calculated "as usual" from $E°$ values in the table, based on $E°_{\text{cell}} = E°_{\text{reduction}} - E°_{\text{oxidation}} = E°_{\text{forward}} - E°_{\text{reversed}}$ with "forward" referring to the half reaction that appears in the forward direction in the table (e.g., Cu^{2+}(aq) + 2 e^- → Cu(s)). If $E°_{\text{cell}} > 0$, then $\Delta_rG° < 0$, and the reaction can be spontaneous under standard conditions.

Students can also easily learn the symbolic cell notation, e.g., Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s), based on the observation that the convention is "like a container, with metals on the outside and solutions inside" and that half reactions are shown in the forward direction (Zn(s) → Zn^{2+}(aq) + $2e^-$, Cu^{2+}(aq) + $2e^-$ → Cu(s)). Next, one can address the obvious question of how the electrolyte concentrations affect the energy and cell voltage, which leads to the Nernst equation. The charge transferred in the process is equal to current × time, i.e., $Q_{ele} = It$, from physics, and $Q_{ele} = nzF$, with ion amount n in moles, ion charge number z, and the Faraday constant F, from chemistry. Setting these expressions for Q_{ele} equal and solving for the time t, amount n of ions transferred, or current I provides answers to many interesting problems such as battery life for a given mass of anode metal, the amount of metal deposited in electroplating, or the required current in electrometallurgy. In short, all conventional topics in electrochemistry follow easily once the initial conceptual obstacles have been removed. The analysis of everyday batteries is also simplified by the energy-based approach. A sample set of numerical problems related to the alkaline battery is presented in the SI.

■ CONCLUSIONS

Electrochemical processes in batteries occur in conjunction with a spontaneous reduction in Gibbs free energy resulting from differences in lattice cohesive energies and ionization free energies (in water) of reactants and products, as confirmed quantitatively for many combinations of metals. For batteries without dissolved ions as reactants or products, the highest cohesive (free) energy per atom often identifies the high-energy species that contains the chemical energy. The analysis shows that *atom transfer* out of the metallic bulk into solution or an oxide is at least as important as electron transfer. While many batteries contain high-energy metals such as Zn or Li, the lead−acid car battery stores its energy in H^+(aq), which can be regarded as part of split H_2O. The conceptually simple energy analysis presented here makes teaching of basic electrochemistry more meaningful and efficient. By helping students become proficient in electrochemistry more quickly, it might even facilitate faster training of the next generation of researchers who will develop improved batteries.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.8b00479.

> Formulas of chemical thermodynamics with electrical work; relations of electrical work, $\Delta_r G^o$, and the cell voltage; a discussion of lattice cohesive energy; a diagram of the "ionization energy in water" for Cu^{2+}; a table of meaningful enthalpies and free energies; calculations of free energies of species in the 1.5 V alkaline battery; numerical problems related to the alkaline battery; details of the lead−acid battery; a calculation of the free energy reduction in a concentration cell; and General Chemistry lecture notes (PDF)

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Notes

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