The Straightforward Route Towards the Theoretical Specific Free Enthalpy of Electrochemical Reactions

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Abstract

This paper outlines a simple yet precise method for identifying the theoretical specific free enthalpy of electrochemical reactions on basis of the ideal gas law, equilibrium thermodynamics and Faraday's law, exploiting the normative role of the standard hydrogen electrode in electrochemistry. The result of this approach are discussed in relation to four battery cell reaction examples: $LiCoO_2/C_6$, $LiFePO_4/C_6$, sodium-sulfur (NAS) and NaCl–Ni (ZEBRA). The agreement between calculated and practical values is near-excellent for even stoichiometries which bespeaks the virtually ideal nature of reversible reactions and the quality of the practical optimization efforts alike. These findings highlight the principal nature of intrinsic thermodynamic limitation to equilibrium mass transfer and its key role towards understanding reversible chemical energy storage in a global sense.

1. Introduction

The ideal gas law is a cornerstone to the conception of natural science and the structure of classic physical chemistry is essentially built on a fundament comprising of the ideal gas law and equilibrium thermodynamics which e.g. shows in the thermodynamic standard state at 1 unit of pressure (and not for example 1013.25 units) or the normative role of the standard hydrogen electrode (SHE) in electrochemistry. A matter of little, if any, recognition is that the ideal gas law provides a means for marking out the intrinsic thermodynamic boundaries to reversible hydrogen mass transfer in equilibrium systems:[1] the reversible transfer of 1 % w/w H by sum formula from a sorbent into the gas phase relates in the ideal hydrogen case to the chemical potential of -12033 J (mol H_2)$^{-1}$ and any ideal hydrogen transfer scales proportionally to the chemical potential gradient between gas and sorbent phase by the mass transfer constant $\mu_{1\%}° = -12033$ J (mol H_2)$^{-1}$ [1 % w/w H]$^{-1}$.

This is derived for hydrogen storage in reversible metal hydrides. Yet due to the universality of thermodynamics, the equilibrium approach's indifference towards the hydrogen sorbent and the normative role of the standard hydrogen electrode (SHE), the principle of intrinsic thermodynamic constraint to mass transfer must be recognizable in electrochemistry, too. Hence it is worthwhile to investigate for how this principle may be worked out and what its relation to practice is like.

2. Methodical Approach

By the ideal gas law, the transfer of 1 % w/w H from a sorbent into the gas phase is linked to the chemical potential $\mu_{1\%}° = -12033$ J (mol H_2)$^{-1}$.[1] For the chemical potential equals molar free enthalpy, this may be translated by Faraday's law $\Delta G° = -z\,\mathrm{F}\,E°$ to an according standard hydrogen potential $E_{1\%H}°$: z is the charge-mol equivalent of the reaction, thus $z_{H2} = 2$ mol, and F is the Faraday constant of 96485.3329 C mol^{-1}; the calculation is shown in equation 1.

$$\mu_{1\%}° = -12033 \text{ J (mol H}_2)^{-1} \text{ [1 \% w/w H]}^{-1} = \Delta G_m° = -z \text{ F E}_{1\%H}° \qquad \textbf{(1)}$$
$$\text{E}_{1\%H}° = 0.06236 \text{ V [1 \% w/w H]}^{-1}$$

That the division of a chemical gas potential μ_{H2} by $\mu_{1\%H}$, both logarithmic quantities, indeed results in direct proportionality is demonstrably true:[1] consequently, dividing a SHE potential $E°$ by $E_{1\%H}°$ yields an according [$\pm\Delta$ % w/w H] as equation 2 shows. That is because Faraday's law may be seen the pendant to the ideal gas law in terms charge and electrical potential, the equivalency of chemical to electrical potential applies for hydrogen is a neutral species.[2]

$$\frac{E°}{E_{1\%H}°} = [\pm\Delta\% \text{ w/w H}] \quad \textbf{(2)}$$

By means of equation 2, the SHE potential excursion featured by the other half-cell can be translated to a hydrogen mass transfer amount in % w/w H: The arithmetic sign convention reflects the sorbent-phase centred model by which $\mu_{1\%H}°$ is defined:[1] a negative $E°$ potential indicates a negative hydrogen mass transfer with regard to the SHE sorbent (HCl), thus towards the gas phase, in line with the common SHE convention. That relative hydrogen mass amount can be alternately expressed by means of a quotient of absolute masses as shown in equation 3a, respective mol number as shown in equation 3b.

$$[\pm\Delta\% \text{ w/w H}] = \frac{\Delta m_{H2}\,[\text{g}]}{100 \text{ g}} \quad \textbf{(3a)}$$

$$\frac{\Delta m_{H2}\,[\text{g}]}{M_{H2}\,100 \text{ g}} = \frac{\Delta n_{H2}}{100 \text{ g}} \quad \textbf{(3b)}$$

In relation to the half cell reaction featuring the potential excursion $E°$, the information about specific hydrogen mol number translates to a corresponding mass amount of the migrating ionic species X via the charge-mol equivalents z_X respective $z_{H2} = 2$ and the molar mass M_X, as equation 4 shows.

$$\frac{\Delta n_{H2}}{100 \text{ g}}\,\frac{z_X M_X}{2} = \frac{\Delta m_X}{100 \text{ g}} \quad \textbf{(4)}$$

The equivalent-mass change Δm_X is expressed in terms of mol number Δn_X by dividing it by M_X which partly reverses (illustrative) equation 4. The expression for the equivalent-mol number Δn_X to hydrogen on basis of equations 3b and 4 thus simplifies as equation 5 shows.

$$\frac{\Delta m_X}{100 \text{ g}}\,\frac{1}{M_X} = \frac{\Delta n_X}{100 \text{ g}} = \frac{\Delta n_{H2}}{100 \text{ g}}\,\frac{z_X}{2} \quad \textbf{(5)}$$

Equation 5 conveys under the premise of ideal equilibrium how many mol of species X can be transferred until the featured SHE potential gradient $E°$ is dissipated: this depends only on charge respective redox equivalents. Equation 6 shows the subsuming of all transformations since equation 2 with $E°$ now being indexed as $E_X°$ in accordance with the above reasoning.

$$\frac{E_X°}{\mathrm{E}_{1\%\mathrm{H}}°}\,\frac{z_X\,\cancel{M_X}}{2\,M_{\mathrm{H2}}}\,\frac{1}{\cancel{M_X}}\ [\mathrm{mol\ g^{-1}}] = \frac{\Delta n_X}{100\ \mathrm{g}}\ [\mathrm{mol\ g^{-1}}] \qquad \mathbf{(6)}$$

Equation 6 can be further simplified if ($2\ M_{\mathrm{H2}}$) is set to a constant of 4 g $(\mathrm{mol})^{-1}$ and a factor 10 is introduced for scaling to the more common kg mass reference as equation 7 shows.

$$\frac{\Delta n_X}{100\ \mathrm{g}}\ [\mathrm{mol\ g^{-1}}] = 10\,\frac{E_X°}{\mathrm{E}_{1\%\mathrm{H}}°}\,\frac{z_X}{4}\ [\mathrm{mol\ g^{-1}}] \qquad \mathbf{(7)}$$

The specific mass transfer in mol of species X is converted by means of Faraday's law into the corresponding specific Gibbs standard enthalpy $\Delta G_{\mathrm{s}}°$ on a charge-mol equivalent basis: equation 8a shows the accordingly transformed expression for $\Delta G_{\mathrm{s}}°$ while equation 8b is its pendant for the common unit of Wh kg^{-1}.

$$\frac{\Delta G°}{1000}\ [\mathrm{J\ g^{-1}}] = -\,\frac{(E_X°{\cdot}z_X)^2}{\mathrm{E}_{1\%\mathrm{H}}°}\,\frac{10\ \mathrm{F}}{4}\ [\mathrm{J\ g^{-1}}] \qquad \mathbf{(8a)}$$

$$\Delta G_{\mathrm{s}}°\ [\mathrm{Wh\ kg^{-1}}] = -\,\frac{(E_X°{\cdot}z_X)^2}{\mathrm{E}_{1\%\mathrm{H}}°}\,\frac{10\ \mathrm{F}}{4{\cdot}3600}\ [\mathrm{Wh\ kg^{-1}}] \qquad \mathbf{(8b)}$$

Equation 8b is an important intermediate result and it is noteworthy that always a negative $\Delta G_{\mathrm{s}}°$ is obtained regardless of the arithmetic sign of $E_X°$ as it must because spontaneous mass transfer at the SHE electrode occurs in both cases. It is subsequently investigated how the fundamental regularity of equation 8b relates further to practice.

3. Results

Equation 8b is applied to the well-known SHE potentials of the redox pairs $\mathrm{Li/Li^+}$ and $\mathrm{Na/Na^+}$,[3] shown in equations 9a and 9b, respectively.

$$\mathrm{Li/Li^+} \qquad E_{(\mathrm{Li/Li^+})}° = -3.040\ \mathrm{V} \quad \Rightarrow \quad \Delta G_{\mathrm{s}}° = -9929.9\ \mathrm{Wh\ kg^{-1}} \qquad \mathbf{(9a)}$$

$$\mathrm{Na/Na^+} \qquad E_{(\mathrm{Na/Na^+})}° = -2.713\ \mathrm{V} \quad \Rightarrow \quad \Delta G_{\mathrm{s}}° = -7908.5\ \mathrm{Wh\ kg^{-1}} \qquad \mathbf{(9b)}$$

These specific free enthalpy (energy if bottled up) values refer to the redox transition of a kg of the respective bare metal: yet their actual proportion in terms of mass is only a fraction of respective battery cell reactions. Thus, application of equation 8b respective 9a or 9b values to a distinct reaction formula requires their adjustment to the respective mass proportion. This yields the specific enthalpy if the SHE potential gradient of $E_X°$ is 100 % dissipated by mass transfer i.e. a complete discharge; equation 10 shows that accordingly.

$$\Delta G_{\mathrm{s}}°\ [\mathrm{Wh\ kg^{-1}}] = -\,\frac{(E_X°{\cdot}z_X)^2}{\mathrm{E}_{1\%\mathrm{H}}°}\,\frac{10\ \mathrm{F}}{4{\cdot}3600}\,\frac{m_X}{m_{\mathrm{reaction}}}\ [\mathrm{Wh\ kg^{-1}}] \qquad \mathbf{(10)}$$

Yet terms and conditions apply to practical electrochemical reversibility; a factor suiting the purist approach while sparing the need for any discussion of deeper causes is the discharge voltages quotient $x = (U_{\mathrm{start,dc}} - U_{\mathrm{cut\text{-}off,dc}}) / U_{\mathrm{output}}$: this factor captures to what extent the base voltage gradient of $E_X°$ is dissipated but expressed in actual battery cell voltage terms. This applies with general validity and in proportion due to the normative role of SHE potentials respective Faraday's law; equation 11 shows the accordingly amendments.

$$\Delta G_s° \,[\mathrm{Wh\ kg^{-1}}] = -\frac{(E_X° \cdot z_X)^2}{\mathrm{E_{1\%H}}°}\,\frac{10\ \mathrm{F}}{4 \cdot 3600}\,\frac{m_X}{m_{\mathrm{reaction}}} \quad [\mathrm{Wh\ kg^{-1}}] \tag{11}$$

The three cell voltages are usually readily available information, e.g. in practice attainable from the data sheet of a commercial battery cell.

Equation 12 shows a prominent secondary Li-battery reaction, comprising of a $LiCO_2$ cathode and a graphite anode: this example is considered on basis of the data for the commercial Panasonic NCR18650B (3.35 Ah) cell with $U_{\mathrm{start,dc}}$ = 4.2 V, $U_{\mathrm{cut\text{-}off,dc}}$ = 2.5 V at U_{output} = 3.6 V, resulting in a factor x = 0.472 in equation 12 This is for determining the graphite amount as affecting the gravimetric proportion of lithium which figures at x = 0.472 to [5.262 % w/w Li].

$$\mathrm{LiCoO_2} + x\,\mathrm{C_6} \rightleftharpoons \mathrm{Li_{(1\text{-}x)}CoO_2} + x\,\mathrm{LiC_6} \tag{12}$$

$$-9929.9\ \mathrm{Wh\ kg^{-1}} \cdot 0.05262 \cdot \frac{4.2\ \mathrm{V} - 2.5\ \mathrm{V}}{3.6\ \mathrm{V}} = -247\ \mathrm{Wh\ kg^{-1}}$$

The battery cell datasheet gives for the reaction at bare cell dimensions a specific energy value of 243 Wh kg^{-1}, in excellent agreement to the calculated value.

Another well-known lithium secondary battery chemistry utilizes $LiFePO_4$ as cathode which is shown in equation 13 in combination with a graphite anode: this example is considered on basis of the data for the commercial AA Portable Power Corp LFP18650-1500 (1.40 Ah) secondary battery cell with $U_{\mathrm{start,dc}}$ = 3.65 V, $U_{\mathrm{cut\text{-}off,dc}}$ = 2.5 V at U_{output} = 3.2 V, resulting in a factor of x = 0.359 in equation 13. Hence this corresponds to a gravimetric proportion of [3.780 % w/w Li] in the sum formula of equation 12.

$$\mathrm{LiFe^{II}PO_4} + x\,\mathrm{C_6} \rightleftharpoons \mathrm{Li_{(1\text{-}x)}Fe^{III}PO_4} + x\,\mathrm{LiC_6} \tag{13}$$

$$-9929.9\ \mathrm{Wh\ kg^{-1}} \cdot 0.03780 \cdot \frac{3.65\ \mathrm{V} - 2.5\ \mathrm{V}}{3.2\ \mathrm{V}} = -135\ \mathrm{Wh\ kg^{-1}}$$

The specific energy of the LFP18650-1500 cell at the nominal capacity of 1.4 Ah figures to 109 Wh kg^{-1} and at the maximum capacity of 1.5 Ah, it is 117 Wh kg^{-1}, on basis of the mass of the encased cell of 41 g. Therefore, the result of equation 13 can be considered in very good agreement, all the more it does not account for any facultative reactant ratio variation.

The sodium-sulfur (NAS) battery reaction is rather complex due to its multiple polysulphide intermediates:[4,5] 100 % depth-of-discharge (DOD) is not defined by reduction of the sulfur electrolyte to Na_2S but Na_2S_3.[6] Yet in practice, the NAS battery cell is often designed to stop discharging at 85 to 90 % of that theoretical capacity due to the corrosive nature of Na_2S_3.[7] The NAS battery shows a stable open circuit voltage (OCV) of 2.075 V up to 59 % DOD, just short of the stoichiometry Na_2S_5 at 60% DOD. Then the OCV drops rather linearly to 1.78 V at the stoichiometry Na_2S_3 respective 100 % DOD.[4,8] In Na_2S_5 amounts the sodium mass proportion to [22.287 % w/w Na], in Na_2S_3 it is [32.340 % w/w Na] accordingly; adjusting to the 60:40 DOD ratio, the sodium mass percentage of the reaction(s) shown in equation 14 is thus [26.3082 % w/w Na], with $U_{\text{start,dc}}$ = 2.075 V, $U_{\text{cut-off,dc}}$ = 1.78 V and U_{output} = 2.075 V.

$$2\ \mathrm{Na} + 0.625\ \mathrm{S_8} \rightleftharpoons \mathrm{Na_2S_5}\ (60\ \%\ \mathrm{DOD}) \qquad \textbf{(14)}$$
$$\mathrm{Na_2S_5} + 2\ \mathrm{Na} + 0.125\ \mathrm{S_8} \rightleftharpoons 2\ \mathrm{Na_2S_3}\ (100\ \%\ \mathrm{DOD})$$

$$-7908.5\ \mathrm{Wh\ kg^{-1}} \cdot 0.263082 \cdot \frac{2.075\ \mathrm{V} - 1.780\ \mathrm{V}}{2.075\ \mathrm{V}} = -296\ \mathrm{Wh\ kg^{-1}}$$

The NGK insulators NAS-cell T5 model represents the alleged pinnacle of this technology; it features a rated voltage of 2.075 V and a rated capacity of 632 Ah at a reactant mass of 5.5 kg.[4,9] These figures yield a nominal specific energy of 238 Wh kg^{-1}; however, the T5 cells are designed to give that value in practice after 2500 cycles and at 81 % DC efficiency.[10] Thus, the specific energy at theoretical 100 % DC efficiency is 294 Wh kg^{-1}.

The reaction of the ZEBRA-battery in the classic NaCl−Ni setup is in its essence shown in equation 15: it features an open circuit voltage (OCV) of 2.58 V, the operational window for 0 to 100 % state of charge (SOC) lies between 1.58 V and 2.58 V.[11] Beyond a SOC of 98 %, there is an overcharge reaction which raises the OCV up to 3.05 V.[4,11] The sodium mass proportion in $(NaCl)_2$−Ni amounts to [26.187 % w/w Na]: equation 15 shows the according calculation with $U_{\text{start,dc}}$ = 2.58 V, $U_{\text{cut-off,dc}}$ = 1.58 V and U_{output} = 2.58 V.

$$\mathrm{Ni} + 2\ \mathrm{NaCl} \rightleftharpoons \mathrm{NiCl_2} + 2\ \mathrm{Na} \qquad \textbf{(15)}$$

$$-7908.5\ \mathrm{Wh\ kg^{-1}} \cdot 0.26187 \cdot \frac{2.58\ \mathrm{V} - 1.58\ \mathrm{V}}{2.58\ \mathrm{V}} = -803\ \mathrm{Wh\ kg^{-1}}$$

The result of 803 Wh kg^{-1} is adjusted to the 98 % SOC limit due to the overcharge reaction,[4,11] which yields 787 Wh kg^{-1}, concisely the theoretical value of Li *et al* (305 Ah kg^{-1} at 2.58 V).[12]

4. Discussion

The specific free enthalpy respective energy of even a multi-step electrochemical reaction as seen for the NAS-battery can be determined with fine precision by means of the outlined approach. From its foundations towards its result, the line of argument is tight; hence there is not really much need for a discussion of the event as such. The founding principle of intrinsic thermodynamic limitation to reversible hydrogen mass transfer may be challenged but can be easily accounted for:[1] the only point meriting special attention is that the division of an ideal gas chemical potential by a calibration standard of the kind, both logarithmic quantities, results in linear proportionality. That builds the bridge to Faraday's law and from there it's all linear relations down the road.

Reversibility as a thermodynamic concept essentially presupposes ideal behaviour and the insights gained from that are insofar fundamental and definite as figuring the as-good-as-it-gets. This work is not concerned with the deeper causes why in practice reversibility of an electrochemical cell reaction is usually confined to merely a fraction of the potential gradient but the form of equation 11 suggests it being the baseline for any consideration of the kind. As such, it is not really a surprise that this ideal general thermodynamic approach applies very well to the subject of reversible chemical energy storage, in contrast to the seemingly matter of fact that its first time outline took until the early 21st century.

Nevertheless, the closeness of practical specific energy values to those obtained by ideal theory is quite astonishing and may be seen an impressive testimony of skilled engineering dedicated to particular purpose. In contrast, this paper presents a simple yet powerful tool wielding which does neither require a high degree of specialization nor even an actual vested interest in the art. Irrespective of the reaction that may evoke, objectively it allows the quick and concise assessment of battery specific energy claims with general validity by means of a few, usually readily available, parameters.

It is from a classic scientific perspective satisfying that reversible energy storage is ultimately all about the fundamental concepts of (physical) chemistry: the ideal gas law, equilibrium thermodynamics, Faraday's law, particle-equivalents in terms of various qualities etc. It also substantiates the understanding of chemistry being an art in its own right, not some auxiliary skill to engineering, physics or medicine pursuits seeking to manipulate matter for particular ends. In conclusion, this is an instructive demonstration for the importance and ultimate advantage of seeking a classic global understanding of a scientific subject somewhat independent of an interest in particular ends: emphasizing the latter over the former may lead eventually to the same result in a specific case but likely at the price of disproportionate effort due to the impoverishment in global meaning and metrics. Thus, it is consequential up to compelling for the end-focused positivist mindset to either deny the existence or belittle the role of both: This paper has the privilege of making that one point about the profound difference in quality of insight and required effort, if positivist utilitarian expediency, which is ultimately a non-expediency, is forfeited as the final philosophy of science.[13]

5. Conclusions

The theoretical specific energy of electrochemical reactions can be precisely determined by an approach combining the ideal gas law, equilibrium thermodynamics and Faraday's law with special regard to intrinsic thermodynamic limitation to reversible mass transfer, exploiting the normative role of SHE potentials to electrochemistry. This is possible because of the essentially ideal nature of reversible reactions; it is noteworthy though that understanding the matter globally from a classic principles vantage point, not one of particular interest, unveiled this simple yet powerful tool of practical value, open to virtually everyone.

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7. Conflicts of interest

There are no conflicts to declare.

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