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Electrolyte Additive Concentration for Maximum Energy Storage in Lead-Acid Batteries

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Abstract: The paper presents a method to assess the effect of electrolyte additives on the energy capacity of Pb-acid batteries. The method applies to any chemically unreactive additive, including suspensions and gels. The approach is thermodynamically based and it leads to the definition of a region of admissible concentrations –the battery's admissible range– where the battery can undergo an indefinite number of charge/discharge cycles without suffering permanent damage. An experimental procedure to determine this range is presented. The obtained results provide a way to assess the potential of electrolyte additives to improve the energy capacity of Pb-acid batteries. The same results also provide a means to determine the additive concentration that produces the maximum energy capacity increase of the battery. The paper closes with an example of application of the proposed approach to a practical case.

Keywords: Pb-acid batteries, electrolyte additives, battery energy capacity, electrolyte additive concentration

1. Introduction

Adding a chemical additive to the electrolyte of a Pb-acid battery may modify the specific energy that the battery can store. This fact has been known since the invention of the battery and it is currently a research topic of great interest to the battery industry. The present paper presents a general method to evaluate the effect of electrolyte additives on the energy capacity of the Pb-acid battery and to determine the best additive concentration to use. The electrolyte additive considered here is quite general. It can be a chemical compound or a mixture of chemicals; a suspension or a gel of the kind used to immobilize the electrolyte. The only restriction is that the additive –whatever it is– does not react chemically with the active components of the battery.

Additives are also added to battery electrolyte for a host of other reasons, such as prolonging battery life, reducing electrode corrosion, improving conductivity, diminishing gas evolution at the electrodes, protecting against overcharging or deep discharging, etc. Quite often, additives that are beneficial in some respects are detrimental in others. Thus, choice and concentration of the additive must always be assessed against the side effects that it produces. This means, in particular, that an additive that enhances the battery's energy capacity may not be viable, at least at certain concentrations, owing to other undesirable effects that it produces.

There are hundred of papers, books and patents dealing with electrolyte additives and their effects in Pb-acid batteries. A complete review of the literature would by far exceed the scope of the present paper. Chapter 3 of Pavlov's book [16] contains a comparatively short review of the main literature on the subject up to about 2011. It concerns classic inorganic additives (phosphoric acid, boric acid, citric acid, strontium sulphate, sodium sulphate), carbon suspensions and organic polymer emulsions. At the present, the great potential of ionic liquids as electrolyte additives is actively studied [17] due to the capacity of these salts to widen the electrochemical window of water [18], [19] and [20]. Also of great practical interest is the study of additives that produce gelled electrolytes, due to their applications in the field of electric locomotion [21], [22] and [23]. An

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interesting paper on the addition of an additive to a gelled electrolyte is presented in a recent paper [24].

The variety of available additives makes it impossible to give general rules on the best additive and best concentration to use for a given purpose. Therefore, the present paper must of necessity be rather restricted in scope. For this reason, by ignoring any other effect, this paper concentrates on the influence of the additives on the energy storage capacity of the battery. The analysis presented provides a general way to asses the effect of any electrolyte additive as far as this capacity is concerned. It also shows how the additive concentration that maximizes this capacity can be determined from a few basic experimental data. Of course a positive assessment of an additive for what concerns the energy capacity of the battery does not rule out the need to ascertain whether and to what extent the additive produces undesired side effects. However, in the search for the best additives to increase the energy storage capacity of a battery, the results of the present paper may help to discard ineffective additives quickly, thus greatly simplifying the selection process.

Central to the analysis of this paper is the observation that at any finite temperature the internal energy of any finite volume system must be finite. This is a consequence of the energy conservation principle or first law of thermodynamics. Under rather broad assumptions, which are met by most natural systems and by electrolyte solutions in particular, this observation together with the second law of thermodynamics implies a limit to the specific free energy that the electrolyte can store and supply isothermally. This point is discussed in Section 3. A similar analysis was previously applied in reference [2] to determine the maximum energy capacity of a living cell –a problem that is conceptually analogous to the one considered here.

The present approach leads to the definition of the battery's limit curve (Section 4). This curve defines the limit concentration of the electrolyte components beyond which the battery suffers irreversible damages, which thus reduce the battery service life. In the case of a Pb-acid battery these damages materialize in evolution of O_2 at the positive electrode for excess of charge, or evolution of H_2 at the negative electrode under deep discharge. The said limit curve is instrumental not only to find out the value of the maximum increase in the battery energy capacity that can be achieved by the use of a given electrolyte additive, but also to determine the value of the additive concentration that produces this maximum increase. It also leads to establish the limits of charge within which no damage is produced for repeated charge and discharge cycles. A practical example of application of the obtained results is given in Section 5.

2. Free energy of battery electrolytes with additives

The free energy of a solution or a mixture is the sum of the free energies of its components. Thus, if $n_{\mathrm{H_2O}}$, $n_{\mathrm{H_2SO_4}}$ and n_{j} (j = 1, 2, …, k) denote respectively the moles of water, the moles of sulphuric acid and the moles of additives, the Gibbs free energy of a Pb-acid battery electrolyte at pressure *p* and absolute temperature *T* is given by:

$$G = G(n_{\mathrm{H_2O}}, n_{\mathrm{H_2SO_4}}, n_1, n_2, \ldots, n_{\mathrm{k}}, p, T) = n_{\mathrm{H_2O}}\ \mu_{\mathrm{H_2O}} + n_{\mathrm{H_2SO_4}}\ \mu_{\mathrm{H_2SO_4}} + \sum_{\mathrm{j=1}}^{\mathrm{k}} n_{\mathrm{j}}\,\mu_{\mathrm{j}} + C\,. \qquad (2.1)$$

Here $\mu_{\mathrm{H_2O}}$, $\mu_{\mathrm{H_2SO_4}}$ and μ_{j} are the partial molar Gibbs free energies or chemical potentials of water, sulphuric acid, and additives, respectively, while *C* is an arbitrary constant. The chemical potential of any component of a solution or mixture can always be expressed in the form:

$$\mu = \mu^{\mathrm{o}}(p^{\mathrm{o}}, T) + \overline{V}\,\Delta p + RT\,\ln a\,. \qquad (2.2)$$

In this equation, μ^{o} is the chemical potential of the considered component in a standard state at pressure p^{o} and temperature *T*, while $\overline{V}$ is the partial molar volume of the same component, *R* is

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the universal gas constant, Δp stands for $p - p^\circ$ and, finally, a is the activity or effective concentration of the considered component.

In what follows, the mole ratio

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{H_2SO_4} + \sum_{j=1}^{k} n_j} \tag{2.3}$$

is taken as a measure of solvent concentration, while the concentrations of sulphuric acid and additives are measured in molalities (moles per kg of H_2O) and denoted by $b_{H_2SO_4}$ and b_j, respectively. That is

$$b_{H_2SO_4} = \frac{n_{H_2SO_4}}{m_{H_2O}} = \frac{n_{H_2SO_4}}{n_{H_2O}\,\mathsf{M}_{H_2O}} \tag{2.4}$$

and

$$b_j = \frac{n_j}{m_{H_2O}} = \frac{n_j}{n_{H_2O}\,\mathsf{M}_{H_2O}}, \tag{2.5}$$

where M_{H_2O}= 18.015 10^{-3} kg mol^{-1} is the molar mass of water. In this notation, the activities of the electrolyte components can be expressed as

$$a_{H_2O} = \gamma_{H_2O}\, x_{H_2O} = \frac{\gamma_{H_2O}\, n_{H_2O}}{n_{H_2O} + n_{H_2SO_4} + \sum_{j=1}^{k} n_j}, \tag{2.6}$$

$$a_{H_2SO_4} = \gamma_{H_2SO_4}\, b_{H_2SO_4} = \frac{\gamma_{H_2SO_4}\, n_{H_2SO_4}}{m_{H_2O}} = \frac{\gamma_{H_2SO_4}\, n_{H_2SO_4}}{n_{H_2O}\,\mathsf{M}_{H_2O}}, \tag{2.7}$$

and

$$a_j = \gamma_j\, b_j = \frac{\gamma_j\, n_j}{m_{H_2O}} = \frac{\gamma_j\, n_j}{n_{H_2O}\,\mathsf{M}_{H_2O}}, \tag{2.8}$$

where γ_{H_2O}, $\gamma_{H_2SO_4}$ and γ_j stand for the appropriate activity coefficients, which in general depend on n_{H_2O}, $n_{H_2SO_4}$ and n_j, besides T and p. By expressing μ_{H_2O}, $\mu_{H_2SO_4}$ and μ_j in form (2.2) and using eqs. (2.6)-(2.8), we can write eq. (2.1) as

$$\begin{aligned} G &= n_{H_2O}\, \mu^o_{H_2O}(p^o,T) + n_{H_2SO_4}\, \mu^o_{H_2SO_4}(p^o,T) + \sum_{j=1}^{s} n_j\, \mu^o_j(p^o,T) + V\Delta p \\ &+ RT\left[n_{H_2O} \ln \frac{\gamma_{H_2O}\, n_{H_2O}}{n_{H_2O} + n_{H_2SO_4} + \sum_{j=1}^{k} n_j} + n_{H_2SO_4} \ln \frac{\gamma_{H_2SO_4}\, n_{H_2SO_4}}{n_{H_2O}\,\mathsf{M}_{H_2O}} + \sum_{j=1}^{k} n_j \ln \frac{\gamma_j\, n_j}{n_{H_2O}\,\mathsf{M}_{H_2O}} \right] + C\,. \end{aligned} \tag{2.9}$$

In writing this equation we used the equation

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$$V = n_{\mathrm{H_2O}} \bar{V}_{\mathrm{H_2O}} + n_{\mathrm{H_2SO_4}} \bar{V}_{\mathrm{H_2SO_4}} + \sum_{\mathrm{j=1}}^{\mathrm{k}} n_{\mathrm{j}} \bar{V}_{\mathrm{j}}\,, \tag{2.10}$$

which relates the partial molar volumes $\bar{V}_{\mathrm{H_2O}}$, $\bar{V}_{\mathrm{H_2SO_4}}$ and $\bar{V}_{\mathrm{j}}$ of the electrolyte components to the electrolyte volume, *V*.

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Helmholtz free energy, Ψ, and Gibbs free energy are related to each other by the well-known equation:

$$\Psi = G - p\,V. \tag{2.11}$$

From this and from eq. (2.9), the Helmholtz free energy of the electrolyte is obtained:

$$\begin{aligned}\Psi = {} & n_{\mathrm{H_2O}}\, \mu^{\mathrm{o}}_{\mathrm{H_2O}}(p^{\mathrm{o}},T) + n_{\mathrm{H_2SO_4}}\, \mu^{\mathrm{o}}_{\mathrm{H_2SO_4}}(p^{\mathrm{o}},T) + \sum_{\mathrm{j=1}}^{\mathrm{s}} n_{\mathrm{j}}\, \mu^{\mathrm{o}}_{\mathrm{j}}(p^{\mathrm{o}},T) - p^{\circ} V \\ & + RT\left[n_{\mathrm{H_2O}} \ln \frac{\gamma_{\mathrm{H_2O}}\, n_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}} + n_{\mathrm{H_2SO_4}} + \sum_{\mathrm{j=1}}^{\mathrm{k}} n_{\mathrm{j}}} + n_{\mathrm{H_2SO_4}} \ln \frac{\gamma_{\mathrm{H_2SO_4}}\, n_{\mathrm{H_2SO_4}}}{n_{\mathrm{H_2O}}\, \mathsf{M}_{\mathrm{H_2O}}} + \sum_{\mathrm{j=1}}^{\mathrm{k}} n_{\mathrm{j}} \ln \frac{\gamma_{\mathrm{j}}\, n_{\mathrm{j}}}{n_{\mathrm{H_2O}}\, \mathsf{M}_{\mathrm{H_2O}}} \right] + C.\end{aligned} \tag{2.12}$$

The above formulae are standard. However, as evident from eq. (2.7), the activity coefficient $\gamma_{\mathrm{H_2SO_4}}$ introduced above refers to the overall concentration of sulphuric acid. This coefficient should be distinguished from the mean activity coefficient of sulphuric acid ions, which may be denoted by $\gamma^{\pm}_{\mathrm{H_2SO_4}}$ and is normally considered in electrochemistry (although less so when dealing with Pb-acid batteries). Using $\gamma_{\mathrm{H_2SO_4}}$ instead of $\gamma^{\pm}_{\mathrm{H_2SO_4}}$ somehow simplifies the formulae that follow, since the details of dissociation of sulphuric acid into ions do not play any explicit role in the present approach. The relationship between the two activity coefficients is:

$$\gamma_{\mathrm{H_2SO_4}} = 4\,(b_{\mathrm{H_2SO_4}})^2\,(\gamma^{\pm}_{\mathrm{H_2SO_4}})^3\,. \tag{2.13}$$

This can be obtained from definition (2.7)1 once $a_{\mathrm{H_2SO_4}}$ is expressed as a function of $\gamma^{\pm}_{\mathrm{H_2SO_4}}$ according to the standard formulae for ionic solutes (see, e.g., [1], Sect. 7.4). Both $\gamma_{\mathrm{H_2SO_4}}$ and $\gamma^{\pm}_{\mathrm{H_2SO_4}}$ depend on $b_{\mathrm{H_2SO_4}}$ and they are better determined from experiment.

An important simplification of eq. (1.12) is obtained by introducing the following equation

$$\sum_{\mathrm{j=1}}^{\mathrm{k}} n_{\mathrm{j}} \ln \frac{\gamma_{\mathrm{j}}\, n_{\mathrm{j}}}{n_{\mathrm{H_2O}}\, \mathsf{M}_{\mathrm{H_2O}}} = n_{\mathrm{add}} \ln \frac{\gamma_{\mathrm{add}}\, n_{\mathrm{add}}}{n_{\mathrm{H_2O}}\, \mathsf{M}_{\mathrm{H_2O}}}\,, \tag{2.14}$$

a proof of which, in a slightly modified form, is given in [2]. In this equation we set:

$$n_{\mathrm{add}} = \sum_{\mathrm{j=1}}^{\mathrm{k}} n_{\mathrm{j}}\,, \tag{2.15}$$

and

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$$\gamma_{\mathrm{add}} = \frac{\mathrm{M}_{\mathrm{H_2O}}}{n_{\mathrm{add}}} \left[\prod_{\mathrm{j=1}}^{\mathrm{k}} \left(\frac{\gamma_{\mathrm{j}}\, n_{\mathrm{j}}}{\mathrm{M}_{\mathrm{H_2O}}} \right)^{n_{\mathrm{j}}} \right]^{\frac{1}{n_{\mathrm{eq}}}}, \tag{2.16}$$

where the symbol Π indicates the product of a sequence, i.e.:

$$\prod_{\mathrm{i=1}}^{\mathrm{k}} \mathrm{y_i} = \mathrm{y_1} \cdot \mathrm{y_2} \cdot \ldots \cdot \mathrm{y_k} \,. \tag{2.17}$$

By rewriting the right-hand side of eq. (2.12) as a sum of two parts and by using eq. (2.14), the Helmholtz free energy of the electrolyte can, quite generally, be expresses as

$$\Psi = \Psi' + \Psi'', \tag{2.18}$$

where functions Ψ' and Ψ'' are given by

$$\begin{aligned} \Psi' &= \Psi'(n_{\mathrm{H_2O}}, n_{\mathrm{H_2SO_4}}, n_1, n_2, \ldots, n_{\mathrm{k}}, p^\circ, T) \\ &= n_{\mathrm{H_2O}}\, \mu^{\mathrm{o}}_{\mathrm{H_2O}}(p^{\mathrm{o}}, T) + n_{\mathrm{H_2SO_4}}\, \mu^{\mathrm{o}}_{\mathrm{H_2SO_4}}(p^{\mathrm{o}}, T) + \sum_{\mathrm{j=1}}^{\mathrm{s}} n_{\mathrm{j}}\, \mu^{\mathrm{o}}_{\mathrm{j}}(p^{\mathrm{o}}, T) + C \end{aligned} \tag{2.19}$$

and

$$\begin{aligned} \Psi'' = \Psi''(n_{\mathrm{H_2O}}, n_{\mathrm{H_2SO_4}}, n_{\mathrm{add}}, p, T) = RT \Bigg[& n_{\mathrm{H_2O}} \ln \frac{\gamma_{\mathrm{H_2O}}\, n_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}} + n_{\mathrm{H_2SO_4}} + n_{\mathrm{add}}} \\ & + n_{\mathrm{H_2SO_4}} \ln \frac{\gamma_{\mathrm{H_2SO_4}}\, n_{\mathrm{H_2SO_4}}}{n_{\mathrm{H_2O}}\, \mathrm{M}_{\mathrm{H_2O}}} + n_{\mathrm{add}} \ln \frac{\gamma_{\mathrm{add}}\, n_{\mathrm{add}}}{n_{\mathrm{H_2O}}\, \mathrm{M}_{\mathrm{H_2O}}} \Bigg] - p^\circ V, \end{aligned} \tag{2.20}$$

respectively. As discussed in the next section, Ψ'' is the part of Ψ that determines the admissible range of the electrolyte. Thus, as far as the determination of this range is concerned, eq. (2.20) enables us to substitute all the electrolyte additives with just one single, fictitious additive of amount n_{add} and activity coefficient γ_{add}. Such an additive will be referred to as the *equivalent additive*.

Equation (2.20) is quite general. It applies to any combination of additives be they liquids, solid suspensions, colloids or any mixture thereof. Irrespective of number and kind of additives, the values of n_{add} and γ_{add} can be determined experimentally by exploiting the fact that, as discussed in the next section, there is a limit to the maximum amount of free energy that in isothermal conditions any finite system can store. The details of the relevant experimental procedure are given in Section 5.

3. Free energy limit of the electrolyte solution

At any given finite temperature, the amount of non-thermal energy that a finite system can store or supply is finite. This is an immediate consequence of 1st law of thermodynamics. It implies a limit to the maximum energy that the system can store. When considered in the light of the 2nd law of thermodynamics, the maximum energy limit entails a restriction on the states that a system can reach without suffering irreversible changes in its constitutive properties. Under rather general assumptions, such restriction defines the region of all the states that the system can reach without suffering irreversible changes in its properties. This region is the (thermodynamically) admissible range of the system. Its boundaries are the system's limit surface.

Consider for instance a piece of an elastic material, say a metal, which for simplicity will be regarded as incompressible. The material breaks or yields plastically (irreversible change) as its stress (a state variable of the system) exceeds the values at which the material attains the maximum amount of strain energy that the material can store. The admissible range is, in this case, the elastic

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range of the material in stress space. A similar behaviour is exhibited by most of real-world systems as the energy that they store is increased. The particular case of solutions, on which we are concerned in this paper, is discussed in detail in reference [2]. Reference [3] provides a systematic introduction on the subject, including general systems.

From classical thermodynamics we know that, at a constant temperature, the amount of non-thermal energy that a system can store or supply equals the change in the Helmholtz free energy of the system. We also know that most systems possess an exhaustion state, at which the system's free energy reaches a minimum. This is the state toward which the system moves when set free from the external actions. For such systems, a limit to the maximum amount of non-thermal energy that they can store or supply means a limit to the maximum value of free energy that they can reach above the free energy of their exhaustion state. Not all the free energy of a system is subjected to thermodynamic limitation, though. For instance, any purely mechanical part of the free energy of a system, say the potential energy due to the system's weight, is not limited by thermodynamics (although it may be limited by geometry and mass). Therefore, when looking for the admissible rage of a system, the part of the system's free energy that it is not bounded by thermodynamics should be ignored.

In the present case, the part of the free energy of the electrolyte that not bounded by thermodynamics is Ψ'. This is apparent from definition (2.19), as Ψ' equals the sum of the free energies of the electrolyte components in their standard state. Thus, Ψ' depends on the amounts of these components ($n_{\mathrm{H_2O}}, n_{\mathrm{H_2SO_4}}, n_1, n_2, ..., n_{\mathrm{k}}$) quite apart from whether they are in solution or separated from each other. Because there is no thermodynamic limit to the amounts of material that can be put together to form a system, there is no thermodynamic limit to the values that Ψ' can assume. The situation is totally different for Ψ''. As eqs. (2.20) and (2.6)-(2-8) should make it evident, Ψ'' depends on the concentration of the above components. Thus, it refers to the energy that these components have as a result of their mutual interaction once they are mixed together. Any thermodynamic limitation to the energy of the electrolyte solution must therefore be a limitation on Ψ'', although the total free energy of the solution is the sum of Ψ'' plus the part of energy, Ψ', that each component carries irrespectively of the presence of the other components.

Actually, it can be verified that Ψ'' is only a small fraction of Ψ. The largest part of the total free energy that a battery can store or supply is due to Ψ' and it comes from the changes in $n_{\mathrm{H_2O}}$ and $n_{\mathrm{H_2SO_4}}$ that are produced by the chemical reactions taking place in the electrolyte. Small as it is, however, Ψ'' determines the admissible range of the electrolyte. As a consequence, Ψ'' sets a limit to the total free energy of the battery, Ψ, because it restricts the range of variation of $n_{\mathrm{H_2O}}$ and $n_{\mathrm{H_2SO_4}}$. A similar situation may also apply to solutions that contain chemically reacting components. For instance, in the case of a living cell, the part of the cytosol free energy that determines the admissible range of the cell is only a fraction of the total free energy of the cytosol [2]. In that case too, a small part of the total free energy of the cytosol sets a limit to the amount of solution components, thus limiting the energy that the living cell can store or release and, hence, its capacity to operate.

To make the following analysis independent of the amount of electrolyte, it is convenient to refer to the molal concentration of Ψ'' per kg of solvent. This energy concentration is denoted by ψ'' and is obtained by dividing both sides of eq. (2.20) by $n_{\mathrm{H_2O}}$ $\mathrm{M_{H_2O}}$ (i.e., by the weight in kilograms of the water contained in the electrolyte):

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$$\psi'' = \psi''(n_{H_2O}, n_{H_2SO_4}, n_{add}, p, T) = \frac{R\,T}{\mathsf{M}_{H_2O}} \left[\ln \frac{\gamma_{H_2O}\, n_{H_2O}}{n_{H_2O} + n_{H_2SO_4} + n_{add}} + \frac{n_{H_2SO_4}}{n_{H_2O}} \ln \frac{\gamma_{H_2SO_4}\, n_{H_2SO_4}}{n_{H_2O}\, \mathsf{M}_{H_2O}} + \frac{n_{add}}{n_{H_2O}} \ln \frac{\gamma_{add}\, n_{add}}{n_{H_2O}\, \mathsf{M}_{H_2O}} \right] - \frac{p^\circ\, \bar{\mathrm{V}}}{\mathsf{M}_{H_2O}}, \tag{3.1}$$

where $\bar{\mathrm{V}}$ is the electrolyte volume per mole of solvent:

$$\bar{\mathrm{V}} = \frac{V}{n_{H_2O}}. \tag{3.2}$$

In both the above equations, n_{H_2O} is a variable because the number of moles of water in the electrolyte varies as the battery charges or discharges.

In what follows, temperature is assumed to be constant. Moreover, the dependence of free energy on p will be ignored, as is usually done in the absence of gaseous phases and, anyway, when operating at constant pressure or nearly so. Thus, if ψ''_{max} is the value that ψ'' attains at the thermodynamic limit mentioned above, the following relation:

$$\psi'' \le \psi''_{max} \tag{3.3}$$

applies to all the states that the electrolyte can reach at the considered temperature. When taken together with eq. (3.1), relation (3.3) defines the admissible range of the electrolyte in the space of variables $n_{H_2O}, n_{H_2SO_4}, n_{add}$. The limit surface of the electrolyte is the boundary to this range:

$$\psi'' = \psi''_{max}\ . \tag{3.4}$$

It is therefore equipotential for ψ'' or Ψ''. (The same surface is not, however, equipotential for the total free energy of the system, or for the part Ψ' of it, as eqs. (2.18) and (2.19) show at a glance).

Though variable, $\bar{\mathrm{V}}$ suffers minor changes (less than about 0.3%) in normal battery operation. As far as the present analysis is concerned, therefore, the term $p^\circ\, \bar{\mathrm{V}} / \mathsf{M}_{H_2O}$ that appears in eq. (3.1) can be treated as a constant. As a consequence, its contribution to ψ'' and ψ''_{max} can to a good approximation be neglected when applying relations (3.3) and (3.4), because addition or subtraction of a constant term to both sides of these relations is immaterial. Accordingly, when determining the admissible range and limit surface of the electrolyte or the limit curve of the battery, we shall henceforth ignore the term $-p^\circ\, \bar{\mathrm{V}} / \mathsf{M}_{H_2O}$ in the far right-hand side of eq. (3.1). With this proviso, the admissible range of the electrolyte can be expressed as:

$$\frac{R\,T}{\mathsf{M}_{H_2O}} \left[\ln \frac{\gamma_{H_2O}\, n_{H_2O}}{n_{H_2O} + n_{H_2SO_4} + n_{add}} + \frac{n_{H_2SO_4}}{n_{H_2O}} \ln \frac{\gamma_{H_2SO_4}\, n_{H_2SO_4}}{n_{H_2O}\, \mathsf{M}_{H_2O}} + \frac{n_{add}}{n_{H_2O}} \ln \frac{\gamma_{add}\, n_{add}}{n_{H_2O}\, \mathsf{M}_{H_2O}} \right] \le \psi''_{max}\ . \tag{3.5}$$

In the three-dimensional space $(n_{H_2O}, n_{H_2SO_4}, n_{add})$ this relation defines the region of all the states that the electrolyte can attain without suffering irreversible changes. The boundary of this region is the limit surface of the electrolyte:

$$\frac{R\,T}{\mathsf{M}_{H_2O}} \left[\ln \frac{\gamma_{H_2O}\, n_{H_2O}}{n_{H_2O} + n_{H_2SO_4} + n_{add}} + \frac{n_{H_2SO_4}}{n_{H_2O}} \ln \frac{\gamma_{H_2SO_4}\, n_{H_2SO_4}}{n_{H_2O}\, \mathsf{M}_{H_2O}} + \frac{n_{add}}{n_{H_2O}} \ln \frac{\gamma_{add}\, n_{add}}{n_{H_2O}\, \mathsf{M}_{H_2O}} \right] = \psi''_{max} \tag{3.6}$$

and it represents a surface in the three-dimensional space mentioned above.

4. Battery's admissible range and limit curve

Not all states of admissible range (3.5) can be accessed by the electrolyte inside a battery. Under normal operating conditions, the battery does not exchange material with the surroundings. In these conditions the total number of molecules of water and sulphuric acid inside the battery remains constant. This is an immediate consequence of the well-known overall reaction that controls the battery operation:

$$\mathrm{Pb(s)} + \mathrm{PbO_2(s)} + 2\mathrm{H_2SO_4(aq)} \rightleftharpoons 2\mathrm{PbSO_4(s)} + 2\mathrm{H_2O}(\mathbf{l}). \tag{4.1}$$

The reaction proceeds from left to right during battery discharge. This produces two molecules of water for every two molecules of sulphuric acid that are consumed. Charging the battery drives the reaction in the opposite direction, thus producing two molecules of sulphuric acid for every two molecules of water consumed. In both cases the sum of $n_{\mathrm{H_2O}}$ and $n_{\mathrm{H_2SO_4}}$ remains constant. At any time of battery's charging or discharging process we have, therefore,

$$n_{\mathrm{H_2O}} + n_{\mathrm{H_2SO_4}} = \overline{n}\,, \tag{4.2}$$

where $\overline{n}$ is a constant. The value of this constant depends on battery preparation and can be determined from the values of $n_{\mathrm{H_2O}}$ and $n_{\mathrm{H_2SO_4}}$ at any time of the battery's life. In particular, let $n^{\mathrm{o}}_{\mathrm{H_2O}}$ and $n^{\mathrm{o}}_{\mathrm{H_2SO_4}}$ be the values of $n_{\mathrm{H_2O}}$ and $n_{\mathrm{H_2SO_4}}$ of the electrolyte to be introduced into the battery. These coincide with the values of $n_{\mathrm{H_2O}}$ and $n_{\mathrm{H_2SO_4}}$ of the electrolyte within the battery as the battery starts operating once filled. The following equation must therefore hold true:

$$\overline{n} = n^{\mathrm{o}}_{\mathrm{H_2O}} + n^{\mathrm{o}}_{\mathrm{H_2SO_4}}\,, \tag{4.3}$$

which fixes $\overline{n}$.

Equation (4.2) can be used to eliminate variable $n_{\mathrm{H_2O}}$ from eqs. (3.5) and (3.6). This reduces the number of independent variables appearing in these equations, thus further restricting the range of states that the electrolyte can attain. More explicitly, by introducing eq. (4.2) into eq. (3.5) we obtain the *battery's admissible range*:

$$\begin{aligned} \frac{R\,T}{\mathsf{M}_{\mathrm{H_2O}}}\Bigg[& \ln \frac{\gamma_{\mathrm{H_2O}}\,(\overline{n} - n_{\mathrm{H_2SO_4}})}{\overline{n} + n_{\mathrm{add}}} + \frac{n_{\mathrm{H_2SO_4}}}{\overline{n} - n_{\mathrm{H_2SO_4}}} \ln \frac{\gamma_{\mathrm{H_2SO_4}}\, n_{\mathrm{H_2SO_4}}}{(\overline{n} - n_{\mathrm{H_2SO_4}})\,\mathsf{M}_{\mathrm{H_2O}}} \\ & + \frac{n_{\mathrm{add}}}{\overline{n} - n_{\mathrm{H_2SO_4}}} \ln \frac{\gamma_{\mathrm{add}}\, n_{\mathrm{add}}}{(\overline{n} - n_{\mathrm{H_2SO_4}})\,\mathsf{M}_{\mathrm{H_2O}}} \Bigg] \le \psi''_{\mathrm{max}}\;. \end{aligned} \tag{4.4}$$

This is the region of plane $(n_{\mathrm{H_2SO_4}}, n_{\mathrm{add}})$ that contains all the states that the electrolyte can attain during normal battery operation without suffering irreversible changes (damages). Its boundary is the *battery's limit curve*. It is obtained by taking the equality sign in relation (4.4):

$$\begin{aligned} \frac{R\,T}{\mathsf{M}_{\mathrm{H_2O}}}\Bigg[& \ln \frac{\gamma_{\mathrm{H_2O}}\,(\overline{n} - n_{\mathrm{H_2SO_4}})}{\overline{n} + n_{\mathrm{add}}} + \frac{n_{\mathrm{H_2SO_4}}}{\overline{n} - n_{\mathrm{H_2SO_4}}} \ln \frac{\gamma_{\mathrm{H_2SO_4}}\, n_{\mathrm{H_2SO_4}}}{(\overline{n} - n_{\mathrm{H_2SO_4}})\,\mathsf{M}_{\mathrm{H_2O}}} \\ & + \frac{n_{\mathrm{add}}}{\overline{n} - n_{\mathrm{H_2SO_4}}} \ln \frac{\gamma_{\mathrm{add}}\, n_{\mathrm{add}}}{(\overline{n} - n_{\mathrm{H_2SO_4}})\,\mathsf{M}_{\mathrm{H_2O}}} \Bigg] = \psi''_{\mathrm{max}}\;. \end{aligned} \tag{4.5}$$

This curve of plane $(n_{\mathrm{H_2SO_4}}, n_{\mathrm{add}})$ delimits the region of all the states that the electrolyte can reach reversibly as it operates inside a battery.

Equations (4.1) to (4.5) apply to Pb-acid batteries containing non-reacting electrolyte additives, i.e., additives that do not react chemically between themselves or with other battery components. Non-reacting additives are commonly used in commercial batteries. As already stated, these are the

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only additives about which we are concerned in this paper. The same equations also apply, in particular, in the absence of electrolyte additives, in which case $n_{\text{add}} = 0$.

A typical limit curve $\psi'' = \psi''_{\max}$, as obtained from eq. (4.5), is represented in Figure 1. The battery's admissible range is the shadowed region within the curve. The amount of additive in the electrolyte remains constant during charge and discharge, because the additive is chemically inactive. Thus, charging or discharging the battery within this range displaces the state of the battery up and down a vertical line $n_{\text{add}} = \text{const}$ in plane of Figure 1. Irreversible changes are produced in the electrolyte if the battery's limit curve is trespassed. More specifically, charging the battery increases $n_{\text{H}_2\text{SO}_4}$ and thus moves the state of the battery upward, say along line AB of Figure 1. The process is reversible as long as the battery state remains within segment AB. However, if point A is trespassed, oxygen evolution takes place at the positive electrode, which makes the process irreversible. A similar situation occurs during discharging. In this case, the discharging process consumes sulphuric acid and the battery state moves downward along line AB. Point B on the battery's limit curve is the limit to reversible discharge. Beyond that point, hydrogen develops at the negative electrode, making any further discharge irreversible. The phenomenon of O_2 and H_2 evolution at the limits of the admissible range is related to the electrochemical windows of water. The reader is referred to the relevant literature for details on the chemical reactions that regulate the electrochemical stability of water in aqueous electrolytes (cf., e.g., [9, Ch. 4], [10, Ch. 2], [11, Ch. 8], [12, Ch. 15], and [13]).

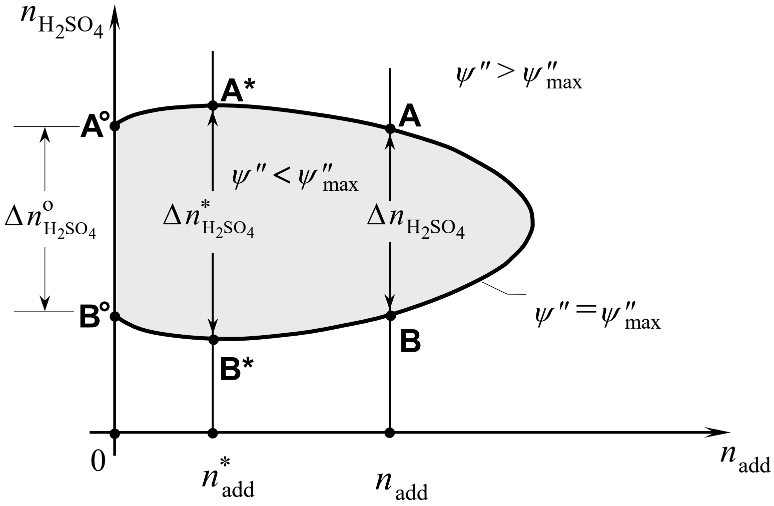

Figure 1. Typical limit curve of a Pb-acid battery containing a non reacting additive in the electrolyte. The curve is obtained from eq. (4.5). The electrolyte does not suffer irreversible changes, if it is kept within the battery's admissible range (shadowed in the figure).

The width of the admissible range along a vertical line through n_{add} is denoted as $\Delta n_{\text{H}_2\text{SO}_4}$ in Figure 1. This width represents the maximum amount of sulphuric acid that, per kilogram of solvent water, can react reversibly according to reaction (4.1). Thus, the greater this width, the greater the amount of energy that the battery can store and produce without deteriorating the electrolyte. The maximum value of $\Delta n_{\text{H}_2\text{SO}_4}$ is attained for $n_{\text{add}} = n^{*}_{\text{add}}$ and it is denoted $\Delta n^{*}_{\text{H}_2\text{SO}_4}$ in the above figure. Because the amount of solvent water depends on the state of charge of the battery, it may be convenient to define additive concentration with reference to a fixed state of charge of the battery.

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This will be taken as the hypothetical state of total discharge, which the battery would attain once all sulphuric acid in the electrolyte is consumed according to reaction (4.1). In this state the amount of water in the electrolyte would be $n_{H_2O} = \overline{n}$, according to eq. (4.2). When referred to this hypothetical state, therefore, the molal concentration of electrolyte additive corresponding to n^*_{add} is given by

$$b^*_{add} = \frac{n^*_{add}}{\overline{n}\ \mathsf{M}_{H_2O}} . \qquad (4.6)$$

This can be considered as the nominal molality of additive that is needed to produce the maximum capacity of energy storage in the battery.

Let $\Delta n^o_{H_2SO_4}$ be the value of $\Delta n_{H_2SO_4}$ when the battery electrolyte is free from additives (cf. Figure 1). Because the energy that a battery can store or supply is proportional to the moles of sulphuric acid which undergo reaction (4.1), the ratio

$$\eta_{max} = \frac{\Delta n^*_{H_2SO_4} - \Delta n^o_{H_2SO_4}}{\Delta n^o_{H_2SO_4}} \qquad (4.7)$$

represents the largest relative increase in the maximum capacity of energy storage that can be obtained from a given electrolyte additive. Of course, η_{max} depends on the additive being used, because so does the battery limit curve.

5. Experimental determination of the limit curve

To determine the limit curve of a battery, we need to know the values of ψ''_{max} and γ_{add} to be introduced into eq. (4.5). These values can be determined experimentally as follows. We start by observing that eq. (4.5) holds true, in particular, when the electrolyte is free from additives. In this case $n_{add} = 0$ and eq. (4 5) reduces to

$$\frac{R\,T}{\mathsf{M}_{H_2O}} \left[\ln \frac{\gamma_{H_2O}\ (\overline{n} - n_{H_2SO_4})}{\overline{n}} + \frac{n_{H_2SO_4}}{\overline{n} - n_{H_2SO_4}} \ln \frac{\gamma_{H_2SO_4}\ n_{H_2SO_4}}{(\overline{n} - n_{H_2SO_4})\,\mathsf{M}_{H_2O}} \right] = \psi''_{max} . \qquad (5.1)$$

This equation applies at the limit of the battery's admissible range. The quantity $\overline{n}$ appearing here is given by eq. (4.3). It depends on battery preparation but not on the presence of electrolyte additives. Thus, by operating on the battery deprived of electrolyte additive, we increase the battery's state of charge until we reach a limit point beyond which oxygen starts to develop at the positive electrode in open circuit conditions (point A° of Figure 1). The appearance of this irreversible phenomenon indicates that the state of the battery has reached the limit curve. We determine the value of $n_{H_2SO_4}$ at this limit and we insert it into eq. (5.1). We can thus calculate ψ''_{max} .

As widely known, sulphuric acid concentration and battery voltage are related to each other (cf., e.g., [4], [5], [6] and [7]). Therefore, rather than determining the above limit value of $n_{H_2SO_4}$, we may determine the maximum open circuit voltage at which the battery maintains its charge without producing oxygen at the positive electrode. This voltage is considerably higher than the theoretical voltage (1.227 V) of water electrolysis [8], owing to the overvoltage that develops at the battery electrodes. The extent of overvoltage depends on the property of the electrode surface and on the presence of small amounts various additives in the electrodes, resulting from their fabrication. As apparent from Section 3, the electrodes themselves do not affect the free energy of the battery electrolyte. However, the overvoltage that they produce influences the battery's admissible range and limit curve, since it affects the limit value $n_{H_2SO_4}$ and, hence, the value of $\psi''_{\max}$. This makes the battery's admissible range and limit curve depend on the properties of the battery as a whole, and not simply on the properties of its electrolyte.

The procedure to determine γ_{add} is analogous to that followed to determine $\psi''_{\max}$. In this case, however, the battery electrolyte should contain a known amount of additive. Again, we charge the battery up to the limit at which oxygen develops at the positive electrode in open circuit conditions. We determine the corresponding value of $n_{H_2SO_4}$ and we insert it together with the considered value of n_{add} into eq. (4.5). Since $\psi''_{\max}$ has already been determined, the only unknown in this equation is γ_{add}, which can thus be determined. Due to the presence of transcendental terms, the value of γ_{add} is best calculated graphically or numerically.

To exemplify, let's refer to a typical car battery at room temperature ($T = 25$ °C = 298,15 K). We assume that, at manufacturing, the electrolyte within the battery contains 1kg of water and a concentration of sulphuric acid of $b^{o}_{H_2SO_4} = 6$ mol/kg (a molal concentration). This means $n^{o}_{H_2O} = 55.51$ mol and $n^{o}_{H_2SO_4} = 6$ mol. Thus, $\overline{n} = 55.51 + 6 = 61.51$ mol, as follows from eq. (4.3). By leavimg the electrolyte free from additives, we charge the battery and find that $b_{H_2SO_4} = 7.25$ mol/kg is the highest sulphuric acid concentration that the battery can maintain in open circuit conditions without producing oxygen at its positive electrode. (This concentration corresponds to a voltage of 2.16 V –or 12.96 V for a six-cell battery– according to the data available from the literature [5]). As observed, battery charge and discharge occurs at constant $\overline{n}$. Therefore, in view of eq. (4.2), we find that the above value $b_{H_2SO_4} = 7.25$ mol/kg means $n_{H_2SO_4} = 7.10$ mol and $n_{H_2O} = 54.41$ mol in the battery electrolyte. By introducing into eq. (5.1) the values of γ_{H_2O} and $\gamma_{H_2SO_4}$ corresponding to this value of $b_{H_2SO_4}$ as available from the literature and reported in the Appendix, and by recalling that $R = 8.3143$ J K^{-1} mol^{-1} and $M_{H_2O} = 18.015 \; 10^{-3}$ Kg mol^{-1}, we calculate that for the battery under consideration $\psi''_{\max} = -20.25$ J kg^{-1}.

To determine γ_{add}, we add an arbitrary amount of the considered additive into the electrolyte of the battery. Let for instance $n_{add} = 5$ mol. By operating on the battery thus modified, we find that the open circuit limit for oxygen evolution at the positive electrode occurs when the battery charge corresponds to an amount of sulphuric acid of, say, $n_{H_2SO_4} = 6.74$ mol. By inserting this value of $n_{H_2SO_4}$ into eq. (5.1), we calculate that $\gamma_{add} = 0.64$, as can be verified from the same equation once we set $n_{add} = 5$ mol, $\overline{n} = 61.51$ mol, and $\psi''_{\max} = -20.25$ J kg^{-1}.

Finally, by inserting these values of $\overline{n}$, $\psi''_{\max}$, and γ_{add} into eq. (5.1) and by making use of the expressions of γ_{H_2O} and $\gamma_{H_2SO_4}$ reported in the Appendix, we obtain the analytic expression of the limit curve of the considered battery. This curve is plotted in Figure 2. From the same figure we find that $\Delta n^{o}_{H_2SO_4} = 5.48$ mol and $\Delta n^{*}_{H_2SO_4} = 6.14$ mol. This implies $\eta_{\max} = 0.12$ according to eq. (4.7). Thus, the electrolyte additive considered in this example can produce up to a 12% increase in the battery's energy storage capacity. The amount of additive needed to produce the maximum energy storage capacity is $n^{*}_{add} = 1.48$ mol, as the figure shows. The corresponding nominal molality of additive is $b^{*}_{add} = 1.34$ mol/kg, according to eq. (4.6).

Different additives may affect the battery differently. For instance, for the same battery considered in the above example, an additive with $\gamma_{\text{add}} = 0.3$ could produce a 25% increase in the energy storage capacity of the battery. This can be checked easily by constructing the limit curve (5.1) for $\gamma_{\text{add}} = 0.3$, relevant to the same values of $\overline{n}$ and $\psi''_{\max}$ given above. In this case the amount of additive producing the maximum energy storage capacity would be $n^*_{\text{add}} = 3.23$ mol, which means $b^*_{\text{add}} = 2.91$ mol/kg.

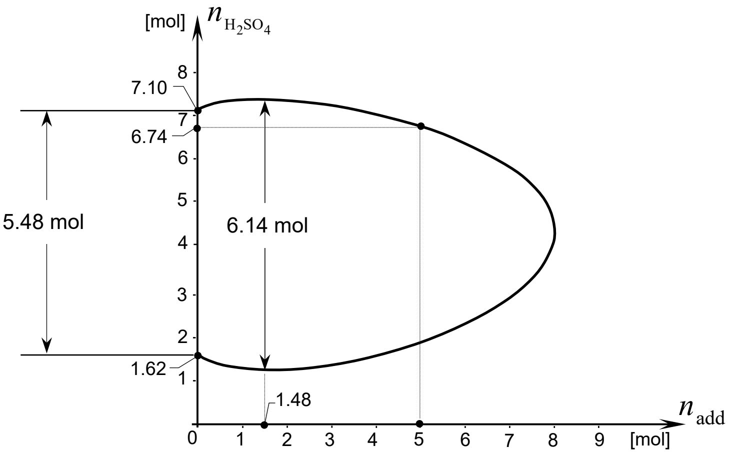

Figure 2. Practical example of battery's limit curve. Because the diagram refers to 1 kg of electrolyte solvent (water), the values reported in the axes can also be read as molal concentrations.

In the above analysis, we treated γ_{add} as a constant, thus neglecting any possible dependence of γ_{add} on additive concentration. This may be acceptable, if the additive concentration is moderately low (as happens in many applications) or if we confine our attention to an sufficiently small portion of the limit curve. Should a better precision be needed, the above procedure to determine γ_{add} could be repeated several times for as many different values of n_{add} as needed. The values of γ_{add} thus obtained could then be used to determine a function $\gamma_{\text{add}}(n_{\text{add}})$ to be introduced for γ_{add} into eq. (5.1), if the approximation $\gamma_{\text{add}} =$ const turns out to be inadequate.

Rather than charging the battery up to the oxygen evolution limit, represented by point A° in Figure 1, we could determine the $\psi''_{\max}$ by discharging the additive-free battery down to point B° of the same figure. This is the point of the battery's limit surface where hydrogen starts to develop in open circuit conditions at the negative electrode of the battery. Once the amount of sulphuric acid corresponding to this lower limit is determined, the procedure is the same as the one already described. Both procedures should provide the same value of $\psi''_{\max}$, because both A° and B° belong to the same curve $\psi'' = \psi''_{\max}$. However, reference to the oxygen evolution limit appears to be more convenient, because hydrogen evolution is a much slower phenomenon.

6. Conclusions

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It is known that the energy capacity of a Pb-acid battery may be influenced by the presence of additives in its electrolyte. The notion of equivalent additive, defined in this paper, helps to analyze the effect of chemically inert additives and mixtures of such additives on the energy capacity of the battery. It can thus be determined an entire region of electrolyte concentrations, referred to as the battery's admissible range, within which no irreversible change or damage is produced in the battery during charge/discharge cycles. The boundary of this region is the battery's limit curve. It corresponds to the concentrations of sulphuric acid, and thus to the range of open circuit voltages, that cannot be exceeded without reducing battery life. The limit curve of a battery can be constructed from a few experiments in which the battery is charged (or discharged) at different additive concentration. It provides useful information about the effectiveness of the additive to increase the energy capacity of the battery, and the best additive concentration to adopt to this end. The practical implications of this for what concerns the choice of the best additive to use are obvious. However, it should be kept in mind that an additive may also produce undesired side effects, which are not considered in the present work and require adequate scrutiny before that any improvement of the energy capacity of the battery resulting from the additive can be considered as practical.

Conflicts of Interest: The author declares no conflict of interest.

Appendix

Activity coefficients of water and sulphuric acid in solution

When expressed in molalities, the concentration of a solute does not depend on the presence of other solutes in the same solution. Moreover, if the concentration of solutes is sufficiently small, the activity coefficient of each solute is only marginally affected by the presence of the other solutes in the same solution. For this reason, in the lack of better data concerning the influence of the addictives on the activity coefficients of the electrolyte, the activity coefficient of sulphuric acid ($\gamma_{\mathrm{H_2SO_4}}$) is assumed to have the same values $\gamma^{\mathrm{o}}_{\mathrm{H_2SO_4}} = \gamma^{\mathrm{o}}_{\mathrm{H_2SO_4}}(b_{\mathrm{H_2SO_4}})$ that it assumes in the absence of additives. In other terms:

$$\gamma_{\mathrm{H_2SO_4}} = \gamma^{\mathrm{o}}_{\mathrm{H_2SO_4}}(b_{\mathrm{H_2SO_4}}) = \gamma_{\mathrm{H_2SO_4}}(n_{\mathrm{H_2O}}, n_{\mathrm{H_2SO_4}})\,, \tag{A.1}$$

where function $\gamma_{\mathrm{H_2SO_4}}(n_{\mathrm{H_2O}}, n_{\mathrm{H_2SO_4}})$ is obtained from $\gamma^{\mathrm{o}}_{\mathrm{H_2SO_4}}(b_{\mathrm{H_2SO_4}})$ after substitution (2.4).

On the other hand, the activity coefficient of a solvent depends on its mole ratio. In the considered case, the solvent is water and its mole ratio, $x_{\mathrm{H_2O}}$, depends on the amounts of sulphuric acid *and* additives contained in the electrolyte, as apparent from definition (2.3). The analysis of present paper, however, concerns unreactive additives at comparatively low concentration. Under these conditions, the influence of additives on solvent activity coefficient, $\gamma_{\mathrm{H_2O}}$, is expected to be of a secondary importance. For this reason and in view of the already mentioned paucity of experimental data, the values of $\gamma_{\mathrm{H_2O}}$ of an electrolyte with additives are assumed to coincide with those of the electrolyte without additives, $\gamma^{\mathrm{o}}_{\mathrm{H_2O}} = \gamma^{\mathrm{o}}_{\mathrm{H_2O}}(x^{\mathrm{o}}_{\mathrm{H_2O}})$. The quantity $x^{\mathrm{o}}_{\mathrm{H_2O}}$ introduced here is the solvent mole ratio when $n_{\mathrm{add}} = 0$. That is:

$$x^{\mathrm{o}}_{\mathrm{H_2O}} = \frac{n_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}} + n_{\mathrm{H_2SO_4}}}\,. \tag{A.2}$$

This assumption on γ_{H_2O} means, therefore,

$$\gamma_{H_2O} = \gamma^{o}_{H_2O}(x^{o}_{H_2O}) = \gamma_{H_2O}(n_{H_2O}, n_{H_2SO_4}) . \tag{A.3}$$

The experimental values attained by functions $\gamma^{o}_{H_2SO_4}(b_{H_2SO_4})$ and $\gamma^{o}_{H_2O}(x^{o}_{H_2O})$ for a wide range of concentrations are reported in many papers and books. For a critical review of these experimental data the reader is referred to [14] and [15]. On the basis of these data, function $(A.4)_1$ is assumed to be approximated by the expression:

$$\gamma_{H_2SO_4} = 2.12^{\,(1.22\, b_{H_2SO_4} - 6.5)} \qquad \mathit{for} \qquad b_{H_2SO_4} \leq 8 \text{ mol/kg} , \tag{A.4}$$

represented graphically in the following figure.

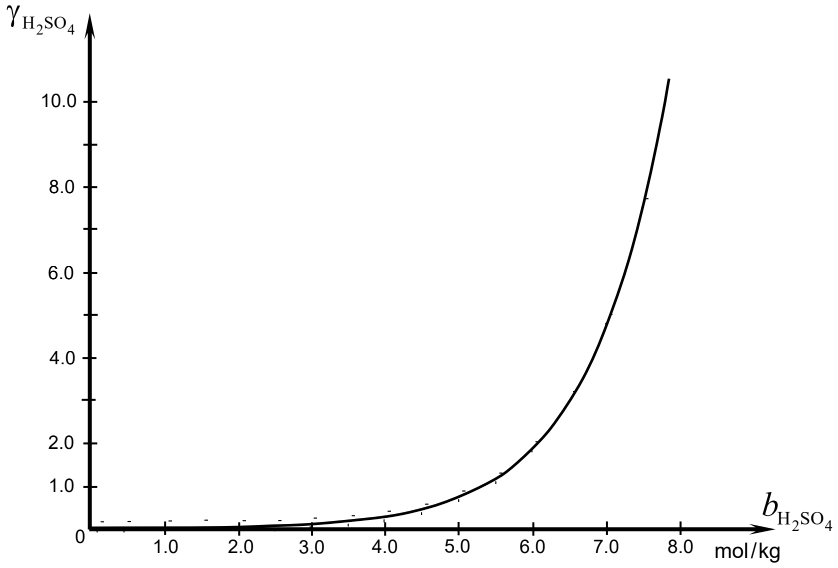

Figure 3. Curve (A.4) showing the dependence of $\gamma_{H_2SO_4}$ on sulphuric acid molality in aqueous solutions. (J) Experimental values of $\gamma^{o}_{H_2SO_4}$, taken from Bullock [15].

As for the solvent, the following polynomial approximation provides a good approximation of well-established experimental data ([14], [15]) concerning the activity of water in sulphuric acid aqueous solutions for $0.4 < x_{H_2O} \leq 1$:

$$\begin{aligned}\gamma_{H_2O} = &- 454.26\, x_{H_2O}{}^{6} + 1699.80\, x_{H_2O}{}^{5} - 2592.82\, x_{H_2O}{}^{4} + 2073.83\, x_{H_2O}{}^{3} \\ &- 919.55\, x_{H_2O}{}^{2} + 214.60\, x_{H_2O} - 20.61 .\end{aligned} \tag{A.5}$$

This equation is plotted in Figure 4 together with the values of $\gamma^{\mathrm{o}}_{\mathrm{H_2O}}$ obtained from the data reported in [15]. Expressions (A.4) and (A.5) were used to determine the battery's limit curve of the example presented in Sect. 5.

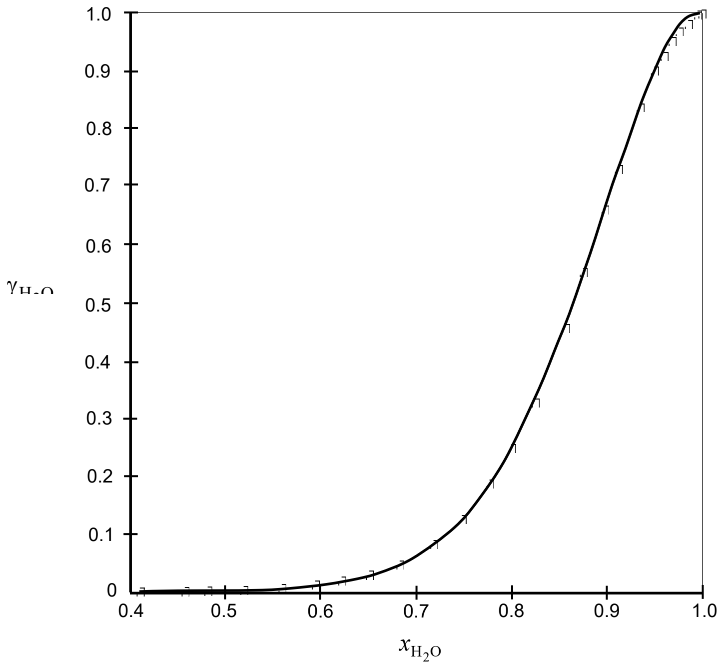

Figure 4. Curve (A.5) showing $\gamma_{\mathrm{H_2O}}$ as a function of $x_{\mathrm{H_2O}}$ for sulphuric acid aqueous solutions. (J) Values of $\gamma^{\mathrm{o}}_{\mathrm{H_2O}}$ calculated from the experimental data reviewed in Bullock [15].

Conflicts of Interest: The author declare no conflict of interest.

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