

Supplementary Materials: Heat to Hydrogen by Reverse Electrodialysis—Using a Non-Equilibrium Thermodynamics Model to Evaluate Hydrogen Production Concepts Utilising Waste Heat

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Variations with electrolyte composition in some thermodynamic and transport properties used in the heat to hydrogen model are here described. Pitzer and coworkers developed semi-empirical expressions relating thermodynamic properties to e.g. solution composition [1], cf. Saluja et al. for a concise overview of these equations [2]. The Pitzer equations are used to model activity and osmotic coefficients, apparent molar enthalpies and apparent molar heat capacities based on experimental data obtained at 25°C. As a simplification, Pitzer parameters for 25°C solutions are also used at 10 and 40°C.

1. The Chemical Potential

The chemical potential of the dissolved salt, μ_e , is the partial derivative of the integral Gibbs free energy, G , for the solution with respect to the moles of dissolved salt, n_e :

$$\mu_e = \left(\frac{\partial G}{\partial n_e} \right)_{n_w, T, p} = \mu_e^0 + \nu RT \ln \left(\frac{m_e \gamma_{\pm}}{m_e^0} \right) \quad (\text{S1})$$

where T is the temperature, R is the gas constant, p is the pressure, n_w is the number of moles of water, n_e is the number of moles of dissolved salt and μ_e^0 is a reference state chemical potential at a molality of m_e^0 where the activity coefficient, γ_{\pm}^0 , is unity [3]. The reference state is denoted by the superscript 0. The stoichiometric coefficient of a monovalent salt is $\nu = (\nu^+ + \nu^-)$, with ν^+ and ν^- being the stoichiometric coefficients for the cation and anion of the salt in the dissolution reaction. The activity model has been applied for a monovalent salt, giving the electrolyte chemical potential in terms of the molality, $(m_e)^\nu = (m_+^{\nu^+} m_-^{\nu^-})$, and the mean activity coefficient $(\gamma_{\pm})^\nu = (\gamma_+^{\nu^+} \gamma_-^{\nu^-})$. In a mixture of dissolved salt and water, the chemical potential of water, μ_w , can be expressed using the osmotic coefficient, φ :

$$\frac{\mu_w - \mu_w^0}{RT} = \ln a_w = -\nu m_e M_w \varphi \quad (\text{S2})$$

where a_w is the water activity and M_w is the molar weight of water in terms of kg mol^{-1} [3]. The chemical potentials of water and the dissolved salt are related through the Gibbs–Duhem equation, and the excess Gibbs energy, G^{ex} , of the single solute in 1 kg of water is [4]:

$$G^{\text{ex}} = \nu m_e RT (1 - \varphi + \ln \gamma_{\pm}) \quad (\text{S3})$$

The activity coefficient and the osmotic coefficient can be expressed using the Pitzer model equations for a single monovalent salt dissolved in water [2]. The Pitzer expressions for the activity coefficient and the osmotic coefficient are then [2]:

$$\varphi - 1 = \frac{-1}{RT m_e} \left(\frac{\partial G^{\text{ex}}}{\partial n_w} \right)_{T, p, n_e} = -A_\varphi \frac{\sqrt{m_e}}{1 + b\sqrt{m_e}} + m_e [\beta_0 + \beta_1 \exp\{-\alpha\sqrt{m_e}\}] + m_e^2 C_\varphi \quad (\text{S4})$$

$$\begin{aligned} \ln \gamma_{\pm} &= \frac{1}{2RT} \left(\frac{\partial G^{\text{ex}}}{\partial n_e} \right)_{T,p,n_w} \\ &= -3A_{\varphi} \left[\frac{2 \ln(1 + b\sqrt{m_e})}{b} + \frac{\sqrt{m_e}}{(1 + b\sqrt{m_e})} \right] \\ &\quad + 2m_e \left[\beta_0 + \beta_1 \left(1 - (1 + \alpha\sqrt{m_e} - \alpha^2 m_e / 2) \exp(-\alpha\sqrt{m_e}) / (\alpha^2 m_e) \right) \right] + \frac{3}{2} m_e^2 C_{\varphi} \end{aligned} \quad (\text{S5})$$

where A_{φ} is the Debye–Hückel slope, $b = 1.2$ and $\alpha = 2$ are constants for monovalent electrolytes, and β_0 , β_1 and C_{φ} are the Pitzer parameters [2]. Parameters fitted to experimental data are required for the estimation of activity and osmotic coefficients, which for KCl is shown in Table S1.

Table S1. Parameters for the activity and osmotic coefficient estimation [1,2], found by regression with tabulated experimental data [5–7].

Salt	β_0	β_1	C_{φ}
KCl	$4.8 \cdot 10^{-2}$	$2.1 \cdot 10^{-1}$	$-8.4 \cdot 10^{-4}$

The Debye–Hückel slope is given by [8]:

$$A_{\varphi} = \frac{1}{3} \left(\frac{2\pi N_A \rho_w}{10^{21}} \right)^{1/2} \left(\frac{e^2 c^2}{DkT} \right)^{3/2} \quad (\text{S6})$$

where N_A is the Avogadro constant, ρ_w is the water (solvent) density, e is the elementary charge, c speed of light in vacuum, D is the dielectric constant of the water solvent and k is the Boltzmann constant. Derivatives of the Debye–Hückel slope with respect to temperature are necessary for the enthalpy and heat capacity calculations. These slopes are [2]:

$$\begin{aligned} A_H &= 4RT^2 \left(\frac{\partial A_{\varphi}}{\partial T} \right)_p \\ A_J &= \left(\frac{\partial A_H}{\partial T} \right)_p \end{aligned} \quad (\text{S7})$$

where A_H and A_J are the slopes for the enthalpy and heat capacity, respectively. The slope values were given by Clarke et al. [8].

2. Enthalpy

By the Gibbs–Helmholtz equation, the partial molar enthalpy, H_e , of the dissolved salt is [3]:

$$H_e = \left(\frac{\partial H}{\partial n_e} \right)_{p,m_e} = -T^2 \frac{\partial}{\partial T} \left(\frac{\mu_e}{T} \right) = H_e^0 - \nu RT^2 \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{p,m_e} \quad (\text{S8})$$

where H_e^0 is the reference state partial enthalpy of the solute. Electrolyte solutions typically use infinite dilution as the reference state, for which $\gamma_{\pm} = 1$ and H_e^0 are, therefore, the partial molar enthalpy at infinite dilution, H_e^{∞} . The quantity $L = H - H^0$ is often referred to as the relative enthalpy, or the excess enthalpy, and can be formulated for the total solution or the individual components. The *total* relative enthalpy of 1 kg of solvent is related to the excess Gibbs energy through the Gibbs–Helmholtz equation [9]:

$$L = H^{\text{ex}} = -T^2 \left(\frac{\partial (G^{\text{ex}}/T)}{\partial T} \right) = \nu m_e RT^2 \frac{\partial}{\partial T} \left(\varphi - \ln \gamma_{\pm} \right)_{p,m_e} \quad (\text{S9})$$

An apparent relative molar enthalpy for the salt, ϕ_L , is typically introduced [9]:

$$\phi_L = \frac{L - n_w L_w^0}{n_e} = \frac{L}{n_e} \quad (\text{S10})$$

where L is the extensive enthalpy of the whole solution relative to infinite dilution, while L_w^0 is the molar enthalpy of the solvent at infinite dilution relative to the reference state, which is zero. The apparent relative molar enthalpy is therefore a quantity which describes any non-ideal behaviour of the dissolved salt. It is related to the integral heat of solution for the dissolving of solid salt in water through:

$$\frac{\Delta_{\text{mix}} H}{n_e} = \Delta_{\text{mix}} H_e^0 + \phi_L \quad (\text{S11})$$

where $\Delta_{\text{mix}} H_e^0$ is the heat of solution per mole of salt at infinite dilution [9]. The solution for extensive enthalpy can be found through:

$$H = n_e \Delta_f H_e + n_w \Delta_f H_w + \Delta_{\text{mix}} H \quad (\text{S12})$$

where $\Delta_f H_i$ is the molar enthalpy of formation for pure component i , and the partial molar enthalpies of the components follow from the derivatives of the extensive enthalpy with respect to the number of moles of that component. The Pitzer model equations for the apparent molar enthalpy were given by Saluja and Pitzer [2]. To ease the notation, it is convenient to introduce the following factors [2]:

$$B = \beta_0 + 2\beta_1 g(\alpha\sqrt{m}) \quad (\text{S13})$$

where the function $g(x)$ is:

$$g(x) = \frac{(1 - (1 + x) \exp(-x))}{x^2} \quad (\text{S14})$$

The apparent molar enthalpy can then be calculated through the following Pitzer model equations [2]:

$$\phi_L = \frac{A_H}{b} \ln(1 + b\sqrt{m}) - 2RT^2 (mB^L + m^2 C_\phi^L) \quad (\text{S15})$$

where the Debye–Hückel slope, A_H , was given in Equation S7, and the factors B^L and C_ϕ^L are given by:

$$\begin{aligned} B^L &= \beta_0^L + 2\beta_1^L g(\alpha\sqrt{m}) \\ \beta_0^L &= \left(\frac{\partial \beta_0}{\partial T} \right)_p & \beta_1^L &= \left(\frac{\partial \beta_1}{\partial T} \right)_p \\ C_\phi^L &= \left(\frac{\partial C_\phi}{\partial T} \right)_p \end{aligned} \quad (\text{S16})$$

In the literature, Pitzer coefficients have been fitted to apparent relative molar enthalpy data, mainly from the heat of dilution experiments. Relevant coefficients and data for KCl are shown in Table S2 [9]. Furthermore, the formation enthalpy of pure solid KCl is $\Delta_f H_e =$

Table S2. Parameters for the apparent relative molar enthalpy estimation from Silvester and Pitzer [9]

Salt	β_0^L	β_1^L	C_ϕ^L
KCl	$5.8 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$-5.1 \cdot 10^{-5}$

$-393.8 \text{ kJ mol}^{-1}$ and for liquid water $\Delta_f H_w = -285.8 \text{ kJ mol}^{-1}$ [10], and the infinite

dilution mixing enthalpy is $\Delta_{\text{mix}}H_e^0 = 17.22 \text{ kJ mol}^{-1}$ [9]. Variations of the vaporisation enthalpy of water in electrolyte solutions were explored in the Pitzer framework by Ge and Wang [11]. A key assumption in this derivation is that the vapour pressure of the solvent is related to the solvent activity:

$$P = a_w P^0 \quad (\text{S17})$$

where P and P^0 are the vapour pressures of the electrolyte solution and the pure solvent at one temperature, respectively. The Clausius–Clapeyron equation is then used to relate the temperature-dependent vapour pressure to the enthalpy of vaporisation:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta_{\text{vap}}H}{R}$$

$$\Delta_{\text{vap}}H = RT^2 \left(\frac{d \ln P^0}{dT} + \frac{d \ln a_w}{dT} \right) \quad (\text{S18})$$

The reader is referred to Ge and Wang for a thorough description of the model equations that arise from these thermodynamic relations [11].

3. Heat Capacity

The partial molar heat capacity, $C_{p,e}$, of the dissolved salt is [3]:

$$C_{p,e} = \left(\frac{\partial H_e}{\partial T} \right)_{p,m_e} = C_{p,e}^0 - \nu R \left(T^2 \frac{\partial^2 \ln \gamma_{\pm}}{\partial T^2} + 2T \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{p,m_e} \quad (\text{S19})$$

where $C_{p,e}^0$ is the reference state heat capacity, or rather the partial molar heat capacity at infinite dilution. The extensive heat capacity of the whole solution, C_p , can be written in terms of the relative enthalpy as [12]:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_{p,m_e} = C_p^0 + \left(\frac{\partial L}{\partial T} \right)_{p,m_e} \quad (\text{S20})$$

where we have that $L/n_e = \phi L$. The apparent molar heat capacity for the salt, $\phi C_{p,e}$, is:

$$\phi C_{p,e} = \frac{C_p - n_w C_{p,w}^0}{n_e} \quad (\text{S21})$$

where $C_{p,w}^0$ is the molar heat capacity of the solvent at infinite dilution. Combining these equations leads to [12]:

$$\phi C_{p,e} = C_{p,e}^0 + \left(\frac{\partial \phi L}{\partial T} \right)_{p,m_e} \quad (\text{S22})$$

The apparent molar heat capacity for the salt can be calculated using Pitzer model equations [2,12]:

$$\phi C_{p,e} = C_{p,e}^0 + \frac{A_J}{b} \ln(1 + b\sqrt{m}) - 2RT^2 (mB^J + m^2 C_{\phi}^J) \quad (\text{S23})$$

where the Debye–Hückel slope, A_J , was given in Equation S7, and the factors B^J and C_φ^J are given by [2]:

$$\begin{aligned} B^J &= \beta_0^J + 2\beta_1^J g(\alpha\sqrt{m}) \\ \beta_0^J &= \left(\frac{\partial\beta_0^L}{\partial T}\right)_p + \frac{2}{T}\beta_0^L & \beta_1^J &= \left(\frac{\partial\beta_1^L}{\partial T}\right)_p + \frac{2}{T}\beta_1^L \\ C_\varphi^J &= \left(\frac{\partial C_\varphi^L}{\partial T}\right)_p + \frac{2}{T}C_\varphi^L \end{aligned} \quad (\text{S24})$$

where the temperature derivative of the apparent relative molar enthalpy for the salt, ϕ^L , was given by Criss and Millero with Pitzer coefficients for KCl shown in Table S3

Table S3. Parameters for the apparent molar heat capacity estimation from Criss and Millero [12]

Salt	β_0^J	β_1^J	C_φ^J
KCl	$1.2 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	$-9.2 \cdot 10^{-7}$

ally, the partial molar heat capacities at infinite dilution for the components are necessary. For KCl we have $C_{p,e}^0 = -114.3 \text{ J K}^{-1}\text{mol}^{-1}$ and for water $C_{p,w}^0 = -75.25 \text{ J K}^{-1}\text{mol}^{-1}$ [10].

4. Density

A first-order linear approximation can be used for the solution density [13]:

$$\rho = \rho_w + \left(\frac{\partial\rho}{\partial m_e}\right)\Delta m_e \quad (\text{S25})$$

where ρ is the solution density, ρ_w is the density of pure water, m_e is the molality and the slope, $(\partial\rho/\partial m_e) = 3.7 \cdot 10^{-2}$, is estimated from experimental data in the literature [5,6].

5. Conductivity

Solution resistances are found using a three-parameter nonlinear model for the electric conductivity, κ , proposed by Zhang et al. [14]:

$$\kappa = k_1 m_e^{k_2} \exp(-k_3 m_e) \quad (\text{S26})$$

where k_1 , k_2 and k_3 are adjustable parameters fitted to experimental data [5–7]. Coefficients for KCl are shown in Table S4

Table S4. Coefficients for the conductivity model found by regression with tabulated experimental data [5–7].

	k_1	k_2	k_3
KCl	9.9	$9.3 \cdot 10^{-1}$	$4.0 \cdot 10^{-2}$

The unit cell resistance, R_{unit} , is calculated as:

$$R_{\text{unit}} = \beta(r_2 + r_1)d_{\text{channel}} + R_{\text{CEM}} + R_{\text{AEM}} \quad (\text{S27})$$

where $\beta = 1.56$ is a shadow factor to account for spacers [13], r_2 and r_1 are the electric resistivities of the concentrate and dilute respectively and R_{CEM} is the area resistance of a CEM and R_{AEM} the area resistance of an AEM.

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