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# How to Set Up Liquid Electrode Reactions

## An Example Using the Standard Hydrogen Electrode

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### 1.0 Introduction and Summary

In order to fully understand the intricacies of implementing electrode reactions within Cantera, there's no substitute for actually carrying the process out on a sample reaction.

The standard hydrogen electrode is the reference electrode used for electrode reaction. Therefore, it's the obvious choice. However, as will be shown in the discussion below, the implementation of the electrode reaction is by no means a simple task, and the actually kinetic parameters to be used in the elementary steps that comprise the reaction are not generally agreed upon, possibly due to their severe dependence on surface preparation issues.

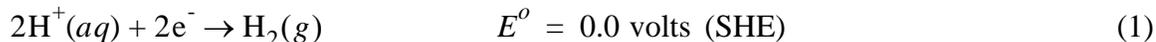
Cantera, however, is demonstrated to have all of the tools necessary to successfully implement what's known about the elementary steps of the reaction and to produce a global reaction rate in the Butler-Volmer format (where it's the appropriate form) that may be used for comparison against experiment. Additionally, with it's emphasis/reliance on elementary steps, Cantera is a good vehicle for providing robust and reproducible links between experimental data and models attempting to reproduce experiment (see ref. [4] for a good example of this).

Below the thermodynamic treatment of the various phases needed to provide a treatment of electrode reactions within Cantera is reviewed. I then present the three reversible elementary reactions which are thought to comprise the Standard Hydrogen Electrode (SHE) electrode kinetics, populate the model with reasonable data, and present the resulting Butler-Volmer global reaction and polarization curves for the reaction.

How this is all implemented within the Cantera framework [1] is the emphasis of this note. Nothing necessarily new has been developed within Cantera to handle electrode reactions. This capability to model Butler-Volmer electrode reactions has previously been used extensively within Cantera to model solid oxide fuel cells [2, 3, 4]. I do, however, explain how this functionality is used within liquid water electrolyte systems.

## 2.0 SHE Electrode Reaction

The half-cell reaction for the standard hydrogen electrode reaction, written in the cathodic direction as required by recent conventions, is defined to be



$E^\circ$ , the standard electrode potential to be defined below, is set to zero by convention at all temperature and pressures for this reaction. The potential difference between two phases can not be readily measured. This is because the measurement always introduces other interfaces which have their own potential difference. Therefore, the (SHE) convention mitigates this problem by creating a relative interphase potential standard against which to compare other electrodes against.

The hydrogen evolution reaction occurs on various electrode materials at greatly varying rates of progress. The fastest and therefore most non-polarizable surfaces on which this reaction occurs are platinum surfaces. One of the slowest surfaces on which this reaction occurs (and therefore most polarizable) is Hg.

The reaction is thought to occur via the following reversible intermediate steps, each of which only involves the transfer of at most one electron. An intermediate of adsorbed hydrogen atoms (on platinum surface sites) is assumed, and calculation of the overall reaction (1) involves solving for the adsorbed hydrogen atom concentration assuming a pseudo-steady state.

The Volmer reaction,



involves the transfer of a proton across the electric double layer to an adsorbed position on the platinum surface, where it combines with an electron. It is considered to be the rate limiting elementary step on platinum-like surfaces.

The Tafel reaction,



involves the reversible recombination of adsorbed hydrogen to form molecular gas-phase Hydrogen.

The Heyrovsky reaction, Eqn. (4), is a competitor to the Tafel reaction, and involves the direct transfer of



a proton across the electric double layer where it reacts with a previously adsorbed hydrogen atom and an electron from the metal to form molecular hydrogen. It's considered to be the rate limiting step for the hydrogen evolution reaction on some other metals such as Hg. There is an

extensive discussion of these reactions in Chapter 8 of Newman's book [12]. Depending upon the identity and construction of the electrode, Newman states that different elementary reactions will be rate limiting. Reaction rate constants for the elementary steps and thermodynamic properties of adsorbates are not given, however.

### 3.0 General Formulation For Equilibrium

Let's say we have an electrode reaction that produces electrons. We will write this in the cathodic direction as Eqn. (5).



$v_i^p$  and  $v_i^r$  (both defined to be always positive) are the stoichiometric coefficients for the products and reactants. The overall stoichiometric coefficient for species  $i$  in the reaction is equal to  $v_i = v_i^p - v_i^r$ .  $M_i$  is the chemical symbol for species  $i$ .

The condition for chemical equilibrium is given by the equilibration of the electrochemical potentials, which we denote by the symbol  $\zeta_i$ :

$$\sum_i^r v_i^r \zeta_i + n \zeta_{e^-} = \sum_i^p v_i^p \zeta_i \quad (6)$$

For uncharged species,  $\zeta_i$  reduces to the value of the chemical potential,  $\mu_i(T, P)$ . If all species participating in the reaction are in the same phase, then the equation above reduces to the standard chemical potential equation, due to charge conservation within the phase. However, if the reaction involves net charge transfer across the interface, then the equation above will also include the potential difference across the interface in its equilibrium expression.

The chemical potential of an electron in a metal,  $\zeta_{e^-}$  (actually any metal), is equal to

$$\zeta_{e^-} = \mu_{e^-}^o + z_{e^-} F \Phi_{\text{electrode}} \quad \text{where } z_{e^-} = -1. \quad (7)$$

In this equation,  $\mu_{e^-}^o$  is nonzero, and because of the SHE potential convention of  $E^o = 0$  at standard state conditions, it must be equal to one half the hydrogen gas standard state chemical potential, a point that is discussed in a very convoluted way in Newman's Chap 2, ref. 12.

$$\mu_{e^-}^o(T, P) = \frac{1}{2} \mu_{\text{H}_2(\text{g})}^o(T, P) \quad (8)$$

A key reason for this is that the standard state chemical potential of the hydrogen ion is defined by convention to be equal to zero at all temperatures and pressures,

$$\mu_{\text{H}^+}^o(T, P) = 0.0 \quad (9)$$

```

<phase dim="3" id="electronPhase">
  <elementArray datasrc="elements.xml"> E </elementArray>
  <speciesArray datasrc="#species_PtH2electrode"> Pt_electron </speciesArray>
  <thermo model="StoichSubstance">
    <density units="g/cm3">2.165</density>
  </thermo>
  <transport model="None" />
  <kinetics model="none" />
</phase>
<!-- species definitions -->
<speciesData id="species_PtH2electrode">
  <species name="Pt_electron">
    <atomArray> E:1 </atomArray>
    <charge>-1</charge>
    <thermo>
      <NASA Tmax="1000.0" Tmin="200.0" P0="100000.0">
        <floatArray name="coeffs" size="7">1.172165560E+00, 3.990260375E-03, -9.739075500E-06,
          1.007860470E-08, -3.688058805E-12, -4.589675865E+02, 3.415051190E-01</floatArray>
      </NASA>
      <NASA Tmax="6000.0" Tmin="1000.0" P0="100000.0">
        <floatArray name="coeffs" size="7">1.466432895E+00, 4.133039835E-04, -7.320116750E-08,
          7.705017950E-12, -3.444022160E-16, -4.065327985E+02, -5.121644350E-01</floatArray>
      </NASA>
    </thermo>
    <density units="g/cm3"> 1.0E-4 </density>
  </species>
</speciesData>

```

**FIGURE 1. XML format for the electron phase within Cantera**

due the charge neutrality constraint creating an essential unmeasurable degree of freedom in liquid phase electrochemistry. This degree of freedom is satisfied by arbitrarily assigning the hydrogen ion to have a zero standard state chemical potential, where the standard state is defined to be the unit molality condition, assuming an ideal molal solution. Therefore, writing down the standard state Gibbs free energy change of reaction for the reaction Eqn. (1),

$$\Delta G_1^o = \mu_{\text{H}_2(\text{g})}^o - 2\mu_{\text{H}^+}^o - 2\mu_{\text{e}^-}^o \quad (10)$$

and applying the relationship between the standard electrode potential and the Gibbs free energy of reaction,

$$\Delta \zeta_1^o = \Delta G_1^o + nFE^o = 0 \rightarrow nFE^o = -\Delta G_1^o, \quad (11)$$

Eqn. (8) is derived.

The electron is assumed to be in its own “phase” within Cantera, because of the form of Eqn. (7). Figure 1 provides the Cantera implementation of this electron phase within a metal. The phase itself is named `electronPhase`, and is defined as a stoichiometric phase, meaning that it consists of one species. It contains one species named `Pt_electron`, with the nontrivial NASA polynomial form necessary to duplicate the one half of the standard state of the hydrogen gas chemical potential, defined using the “zero enthalpy of elements in their natural state” basis ( $H^o(298 \text{ K}, \text{H}_2(\text{g}), 1 \text{ bar}) = 0.0$ ) used by NIST [6], CODATA [7], Chemkin [8] and the JANAF [9] tables. See previous memos for a more complete explanation of the specification of consistent bases [10] for

```

<phase dim="3" id="h2gas">
  <elementArray datasrc="elements.xml">H</elementArray>
  <speciesArray datasrc="#species_data">H2</speciesArray>
  <state>
    <temperature units="K">300.0</temperature>
    <pressure units="Pa">101325.0</pressure>
  </state>
  <thermo model="IdealGas" />
  <kinetics model="none" />
  <transport model="Mix" />
</phase>
<speciesData id="species_data">
  <species name="H2">
    <atomArray>H:2</atomArray>
    <thermo>
      <NASA Tmax="1000.0" Tmin="200.0" P0="100000.0">
        <floatArray name="coeffs" size="7">2.344331120E+00, 7.980520750E-03, -1.947815100E-05,
          2.015720940E-08, -7.376117610E-12, -9.179351730E+02, 6.830102380E-01</floatArray>
      </NASA>
      <NASA Tmax="6000.0" Tmin="1000.0" P0="100000.0">
        <floatArray name="coeffs" size="7">2.932865790E+00, 8.266079670E-04, -1.464023350E-07,
          1.541003590E-11, -6.888044320E-16, -8.130655970E+02, -1.024328870E+00</floatArray>
      </NASA>
    </thermo>
  </species>
</speciesData>

```

**FIGURE 2. XML description of the Hydrogen Gas Phase**

presentation of the chemical potentials of species in gas and electrolyte phases and for an explanation of how to convert between the NIST convention and other conventions such as those used in SUPCRT92 [20].

The chemical potential of species  $i$  in phase  $a$ , where  $a$  may be the electrode, the solution, or the interface between the two, is equal to

$$\zeta_i = \mu_i(T, P, x_i) + z_i F \Phi_a. \quad (12)$$

Note,  $\mu_i(T, P, x_i)$  may have multiple formats. For example it may be a stoichiometric phase, such as an oxide, it may be an ideal solution on the mole fraction basis, or it may be an electrolyte solution, whose activities are defined on the molality scale [2] and whose solute standard states are defined at unit molality assuming an ideal molal solution:

$$\mu_i = \mu_i^\Delta(T, P) + RT \ln(m_i \gamma_i^\Delta), \text{ where } m_i = \frac{n_i}{\tilde{M}_o n_o} \text{ and } \tilde{M}_o = \frac{M_o}{1000} \quad (13)$$

The  $\Delta$  symbol signifies that the standard state and the activity coefficients are on the molality scale.

The hydrogen gas phase is given by Figure 2. It's a pure ideal gas with one species.

Let's expand the electrochemical potentials in Eqn. (6) using Eqn. (12) to develop an expression for equilibrium of the electrode reaction.

$$\sum_i^r v_i^r \mu_i + \sum_i^r v_i^r z_i F \Phi_i + n \mu_{e^-}^o - n F \Phi_{\text{electrode}} = \sum_i^p v_i^p \mu_i + \sum_i^p v_i^p z_i F \Phi_i \quad (14)$$

Collecting terms results in

$$\sum_i^r v_i^r z_i F \Phi_i - \sum_i^p v_i^p z_i F \Phi_i - n F \Phi_{\text{electrode}} = \sum_i^p v_i^p \mu_i - \sum_i^r v_i^r \mu_i - n \mu_{e^-}^o \quad (15)$$

The rhs of Eqn. (15) is the  $\Delta G$ , the Gibbs free energy of reaction.  $\Phi_i$  is the potential of the phase in which species  $i$  belongs. Cantera allows each phase to potentially have its own potential. However, to simplify the lhs of Eqn. (15), we will make the assumption that all charged species are reactants are located in the electrolyte solution phase. Therefore,  $\sum_i^r v_i^r z_i = n$ . And, we may define the potential difference between the electrode and solution phase as  $E$ :

$$E = \Phi_{\text{electrode}} - \Phi_{\text{soln}} \quad (16)$$

Then, Eqn. (15) simplifies to

$$-nFE = \sum_i^p v_i^p \mu_i - \sum_i^r v_i^r \mu_i - n \mu_{e^-}^o = \Delta G \quad (17)$$

We may separate the Gibbs free energy of reaction out into its standard state contribution,  $\Delta G^o$ , defining an equivalent standard potential,  $E^o$ , based on  $\Delta G^o$ ,

$$-nFE^o = \sum_i^p v_i^p \mu_i^o - \sum_i^r v_i^r \mu_i^o - n \mu_{e^-}^o = \Delta G^o, \quad (18)$$

and the deviation from the standard state contribution,  $\Delta G - \Delta G^o$ :

$$-nF(E - E^o) = \Delta G - \Delta G^o \quad (19)$$

The later may be rewritten as:

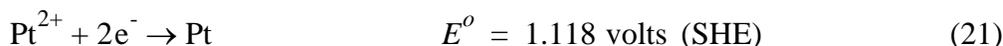
$$E = E^o - \frac{(\Delta G - \Delta G^o)}{nF} \quad (20)$$

which is recognized as the Nernst equation for the reaction, after  $\Delta G - \Delta G^o$  is written out in terms of the logs of the activity coefficients.

$E^o$  is ubiquitously tabulated in standard references such as the CRC. There are several issues to note, in using these tabulations.  $\mu_{e^-}^o$  must be appropriately recognized as being equal to  $1/2 \mu_{\text{H}_2(\text{g})}^o(T, P)$ . Also, the standard state for species in the aqueous electrolytes is defined to be one at which the species is at unit molality in an ideal molal solution state.  $E^o$  is used as an alternative

tabulation of the standard-state Gibbs free energy of formation for ionic species, albeit at only one temperature and pressure.

$E^o$  may be thought of as the barrier in voltage that must be built up in order for a reaction, which would normally want to go forwards spontaneously, i.e.,  $\Delta G < 0$ , to instead be at equilibrium. For example, the noble metals have very high values of  $E^o$ . Eqn. ( ) is an example of a noble metal standard electrode potential reaction.



In the reaction, there is a very strong driving force in the cathodic reaction, i.e., the direction involving the reduction of the metal and the loss of the electron. Therefore, in order for the reaction to be at equilibrium a very high compensating potential  $E$  must be built up in the metal, which tends to drive the creation of electrons in metals, because it makes the chemical potential of electrons lower -see Eqn. (7).

Typically,  $E^o$  values are tabulated in terms of the overall global reaction stoichiometry, which may hide the fact that there are intermediate elementary reaction steps and intermediate species that must be defined. The hydrogen electrode reaction is found to occur via an adsorbed intermediate, which forms a Langmuir-Hinshelwood adsorbate on the platinum catalyst. The Cantera implementation of this surface phase is given in Figure 3. The phase is called `platinum_surface`, and consists of two species, `pt_site`, and `H*_site`. The thermodynamics model is named `surface`, which implements an ideal solution model for the adsorbate phase. This surface model is similar to models which have been used in Cantera to treat surface site compositions for solid oxide fuel cells and diamond growth in CVD systems. The surface site density must be specified. Here, we use a typical value used in the analyses above,  $3 \times 10^{-9} \text{ gmol cm}^{-2}$ , to fill in this number, not having an actual estimated number to go by. The thermodynamics of the adsorbates must also be specified. Again, we must guess at the numbers. We use the `const_cp` formulation for the standard states of the adsorbate species, because it is the simplest. With this formulation we only need to specify  $H^o(T_o)$ ,  $S^o(T_o)$ , and  $C_p^o(T_o)$  at a single temperature  $T_o$ . Because we don't know the thermodynamics of these adsorbate species, using the simplest formulation is prudent. The thermodynamics of adsorbate species will affect the Gibbs free energies of reaction of the reactions in the mechanisms, and thus the reverse rate constants of these reactions. The relative values between the `H*_site` species, a single hydrogen adatom adsorbed onto a base site, and the `pt_site` species, a bare site, will determine the degree of binding energy of hydrogen adsorbed onto the bare platinum metal. An early literature value of  $10 \text{ kcal gmol}^{-1}$  for the hydrogen molecular adsorption on Hg motivates the magnitude of the relative differences in enthalpies between the `pt_site` and `H*_site` values [19]. The binding energy has a large effect on the observed Tafel slope when the `H*_site` surface site fractions become significant. The numbers, however, should be considered to be speculative without a thorough investigation.

## 4.0 Cantera's Implementation of Interfacial Kinetics

The interfacial kinetics object is initiated in the XML element called `phase` by the addition of the `kinetics` XML element (see Figure 3). The attribute `model id` of `Interface` indicates that the object `InterfaceKinetics` should be constructed to handle the calculation of the rates of

progress of reactions defined on the interface and the species source terms for species in bulk and surface phases at or adjacent to the interface. The object automatically includes the interface species in its list of species that may be reactants and products of reactions defined in it, as all reactions may be considered to be located on the interface. In addition, the XML element called `phaseArray` defines other phases which are present at the interface (or on either side of it) and whose species may also be reactants and/or products in reactions. For the particular case of Hydrogen evolution on a platinum electrode, three additional bulk phases are needed to be present at the electrode and defined within the `InterfaceKinetics` object: `Pt_H2electrons` which are electrons in the platinum metal, `NaCl_electrolyte` which is the name of the liquid water electrolyte obeying the Pitzer formulation for specification of the molality-based activities, and `H2gas` which corresponds to pure Hydrogen gas bubbles injected over the platinum metal. The species in these phases are all added into the species vector within the `InterfaceKinetics` object. The actual platinum metal isn't involved in the reaction.

```
<phase dim="2" id="platinum_surface">
  <elementArray datasrc="elements.xml">H E</elementArray>
  <speciesArray datasrc="#species_PtH2electrode">pt_site H*_site</speciesArray>
  <state>
    <temperature units="K">300.0</temperature>
    <coverages>pt_site:0.9 H*_site:0.1</coverages>
  </state>
  <thermo model="Surface">
    <site_density units="mol/cm2"> 3e-09 </site_density>
  </thermo>
  <kinetics model="Interface" />
  <reactionArray datasrc="#reaction_data" />
  <transport model="None" />
  <phaseArray>Pt_H2electrons NaCl_electrolyte h2gas</phaseArray>
</phase>

<speciesData id="species_PtH2electrode">

<!-- species pt_site -->
  <species name="pt_site">
    <atomArray />
    <thermo>
      <const_cp Tmax="5000.0" Tmin="100.0">
        <t0 units="K">298.15</t0>
        <h0 units="kJ/mol">0.0</h0>
        <s0 units="J/mol/K">0.0</s0>
        <cp0 units="J/mol/K">0.0</cp0>
      </const_cp>
    </thermo>
  </species>

<!-- species H*_site -->
  <species name="H*_site">
    <atomArray>H:1</atomArray>
    <thermo>
      <const_cp Tmax="5000.0" Tmin="100.0">
        <t0 units="K">298.15</t0>
        <h0 units="kJ/mol">-21.0</h0>
        <s0 units="J/mol/K">63.0</s0>
        <cp0 units="J/mol/K">10.0</cp0>
      </const_cp>
    </thermo>
  </species>
</speciesData>
```

**FIGURE 3. XML data for the Pt Surface Phase, where the interfacial reaction is located**

In Figure 3, the `reactionArray` XML object defines where to look in the XML file for the reactions defined at the interface. The attribute `datasrc` defines the id of the `reactionData` XML element to look for the reactions. Figure 4 contains the `reactionData` XML element with the matching id of `reaction_data`, where the three Hydrogen electrode reactions are listed. The reactions are in standard Cantera format (see <http://www.cantera.org>). One addition is the `electrochem` XML element with the attribute `beta`. The next section will describe how this  $\beta^e$  changes the reaction rates.

## 5.0 Formulation of the Kinetics in Terms of Elementary Steps

Cantera's implementation of kinetics involving charge transfer reaction is based on the following equation for the forward and reverse reaction rate coefficients for Rxn (5) given by Eqn. (22).

```
<reactionData id="reaction_data">
  <!-- reaction 0001 Volmer reaction - rate limiting -->
  <reaction reversible="yes" type="surface" id="0001">
    <equation>H+ + Pt_electron + pt_site [=] H*_site</equation>
    <rateCoeff>
      <electrochem beta="0.5" />
      <Arrhenius>
        <A>1.1180000E+5</A>
        <b>0.0</b>
        <E units="kJ/mol">40.000000</E>
      </Arrhenius>
    </rateCoeff>
    <reactants>H+:1.0 Pt_electron:1.0 pt_site:1.0</reactants>
    <products>H*_site:1.0</products>
  </reaction>
  <!-- Tafel reaction - fast -->
  <reaction reversible="yes" type="surface" id="0002">
    <equation>2 pt_side + H2 [=] 2 H*_site</equation>
    <rateCoeff>
      <Arrhenius>
        <A>1.900000E+13</A>
        <b>0.0</b>
        <E units="kJ/mol">10.000000</E>
      </Arrhenius>
    </rateCoeff>
    <reactants>pt_side:2.0 H2:1.0</reactants>
    <products>H*_site:2.0</products>
  </reaction>
  <!-- Heyrovsky reaction - set to slow here -->
  <reaction reversible="yes" type="surface" id="0003">
    <equation>pt_side + H2 [=] H*_site + H+ + Pt_electron</equation>
    <rateCoeff>
      <Arrhenius>
        <A>6.000000E-5</A>
        <b>0.0</b>
        <E units="kJ/mol">30.000000</E>
      </Arrhenius>
    </rateCoeff>
    <reactants>pt_side:1.0 H2:1.0</reactants>
    <products>H*_site:1.0 H+:1.0 Pt_electron:1.0</products>
  </reaction>
</reactionData>
```

**FIGURE 4.** Cantera's XML description of the rate constants for the Hydrogen electrode reaction

$$k_f = A_f T^{\beta_f} \exp\left[\frac{-E_f}{RT}\right] \exp\left[\frac{-\beta^e F \left(\sum_k \nu_k z_k \Phi_k\right)}{RT}\right] = k_f^c \exp\left[\frac{-\beta^e F \left(\sum_k \nu_k z_k \Phi_k\right)}{RT}\right] \quad (22)$$

$k_f^c$  is the “chemical part of the rate coefficient.  $\beta^e F \left(\sum_k \nu_k z_k \Phi_k\right)$ , which includes the electron term, may be thought of as the change in the activation energy barrier (or the relative transition state energy level) due to the potential energy difference between the products and reactants in the reaction. The motivation for the form is based on transition state theory applied to electron transfer reactions and is supplied in several standard electrochemistry books (see ref. 18, 16).  $\beta^e$  is the symmetry factor for the transition state, and is an additional input parameter for electron transfer reactions.

Let’s take a look at this term for the case of the Volmer Reaction, Eqn. (2). In this case

$$\sum_k \nu_k z_k \Phi_k = n(\Phi_{\text{metal}} - \Phi_{\text{soln}}) = nE$$

The forward reaction, which is the cathodic direction, is reduced for positive values of  $E$ , and enhanced for negative values of  $E$ . This makes sense, high values of  $\Phi_{\text{metal}}$  stabilize the presence of electrons in the metal by reducing the chemical potential of electrons.

The reverse direction may be calculated from the electrochemical equilibrium constant, which includes the electrical potential energy term in Eqn. (12):

$$\sum_k \nu_k \xi_k = 0. \quad (23)$$

Expanding the terms in Eqn. (23),

$$\Delta G_R^o + RT \ln \left[ \frac{\prod_k a_k^{\nu_k^p}}{\prod_k a_k^{\nu_k^r}} \right] + F \sum_k \nu_k z_k \Phi_k^{eq} = 0, \quad (24)$$

where  $\Delta G_R^o$  is the standard Gibbs free energy of the reaction, the last term on the rhs may be solved for  $E$ , the equilibrium value of the potential drop across the interface, that would induce an equilibrium condition for the elementary reaction. Eqn. (24) can be rewritten as

$$\frac{\prod_k a_k^{\nu_k^p}}{\prod_k a_k^{\nu_k^r}} = \exp\left[\frac{-\Delta G_R^o - F \sum_k \nu_k z_k \Phi_k^{eq}}{RT}\right] = \exp\left[\frac{-\Delta G_R^o - FnE}{RT}\right] \quad (25)$$

where

$$E = \Phi_{\text{metal}}^{eq} - \Phi_{\text{soln}}^{eq}$$

The numerator in Eqn. (25) is a multiplication over the products of the reaction, while the denominator is a multiplication over the reactants of the reaction. We may formulate the reverse rate constant by considering Cantera's treatment of the forward rate of progress of the reaction as

$$ROP_f = k_f \left( \prod_k (c_k^a)^{v_k^r} \right), \quad (26)$$

where  $c_k^a$  are the activity concentrations of the reactant species  $k$ , ( $c_k^a = c_k^s a_k$ , where  $c_k^s$  is the standard concentration and  $a_k$  is the activity of species  $k$ ), with the expression for the reverse rate of progress of the reaction based on mass action kinetics,

$$ROP_r = k_r \left( \prod_k (c_k^a)^{v_k^p} \right), \quad (27)$$

to generate an expression for  $k_r$  that is consistent with electrochemical equilibrium, Eqn. (25).

$$ROP_r = k_f^c \left( \frac{\prod_k (c_k^s)^{v_k^r}}{\prod_k (c_k^s)^{v_k^p}} \right) \exp \left[ \frac{[\Delta G_R^o + (1 - \beta^e) F \sum_k v_k z_k \Phi_k]}{RT} \right] \left( \prod_k (c_k^a)^{v_k^p} \right) \quad (28)$$

When the electric potential drop across the interface is at the equilibrium value,  $nE = \sum_k v_k z_k \Phi_k^{eq}$ , the forward rate of progress and reverse rate of progress are equal. However, the potential drop across the interface may not be at equilibrium and will not be for finite currents crossing the interface electrode. Define this difference as the surface overpotential  $\eta_s$ .

$$n(\Phi_{\text{metal}} - \Phi_{\text{soln}}) = n(E + \eta_s) = \sum_k v_k z_k \Phi_k \quad (29)$$

The surface overpotential  $\eta_s$  represents the departure from the equilibrium potential at the specific conditions of the electrode (including the calculation of the activities) and it is also given by the expression:

$$Fn\eta_s = -n\zeta_e^- + \sum_i^p v_i^p \zeta_i - \sum_i^r v_i^r \zeta_i. \quad (30)$$

Note, we have defined  $\eta_s$  away from the standard state conditions where all unity activities are assumed, and even irrespective of equilibrium conditions. Therefore it's valid under any circumstance, especially one in which there is a net current flowing across the interface.

The forward and reverse rates of progress may be reorganized so that the Butler-Volmer form of the equation is generated. Following the derivation in [4], the forward rate of progress is expressed as:

$$\begin{aligned} ROP_f &= k_f^c \exp\left[\frac{-\beta^e Fn(E + \eta_s)}{RT}\right] \left(\prod_k (c_k^a)^{v_k^r}\right) \\ &= k_f^c \exp\left[\frac{-\beta^e FnE}{RT}\right] \left(\prod_k (c_k^a)^{v_k^r}\right) \left(\exp\left[\frac{-\beta^e Fn\eta_s}{RT}\right]\right) \end{aligned} \quad (31)$$

Then,

$$\begin{aligned} ROP_r &= k_f^c \left(\frac{\prod_k (c_k^s)^{v_k^r}}{\prod_k (c_k^s)^{v_k^p}}\right) \exp\left[\frac{\Delta G_R^o + (1 - \beta^e)Fn(E + \eta_s)}{RT}\right] \left(\prod_k (c_k^a)^{v_k^p}\right) \\ &= k_f^c \left(\frac{\prod_k (c_k^s)^{v_k^r}}{\prod_k (c_k^s)^{v_k^p}}\right) \left(\frac{\prod_k a_k^{v_k^r}}{\prod_k a_k^{v_k^p}}\right) \exp\left[\frac{(1 - \beta^e)Fn\eta_s - \beta^e FnE}{RT}\right] \left(\prod_k (c_k^a)^{v_k^p}\right) \\ &= k_f^c \exp\left[\frac{-\beta^e FnE}{RT}\right] \left(\prod_k (c_k^a)^{v_k^r}\right) \left(\exp\left[\frac{(1 - \beta^e)Fn\eta_s}{RT}\right]\right) \end{aligned} \quad (32)$$

Then, the net rate of progress for the reaction may be written as

$$RO P_{net} = k_f^c \exp\left[\frac{-\beta^e FnE}{RT}\right] \left(\prod_k (c_k^a)^{v_k^r}\right) \left(\exp\left[\frac{(1 - \beta^e)Fn\eta_s}{RT}\right] - \exp\left[\frac{(1 - \beta^e)Fn\eta_s}{RT}\right]\right) \quad (33)$$

Eqn. (25) may be used to eliminate  $E$  from the Eqn. (33).

$$\exp\left[\frac{-\beta^e FnE}{RT}\right] = \left(\frac{\prod_k (c_k^a)^{v_k^p \beta^e}}{\prod_k (c_k^a)^{v_k^r \beta^e}}\right) \left(\frac{\prod_k (c_k^s)^{v_k^r \beta^e}}{\prod_k (c_k^s)^{v_k^p \beta^e}}\right) \exp\left[\frac{\beta^e \Delta G_R^o}{RT}\right] \quad (34)$$

to yield

$$\begin{aligned}
ROP_{net} = k_f^c & \left( \prod_k^r (c_k^a)^{v_k^r(1-\beta^e)} \right) \left( \prod_k^p (c_k^a)^{v_k^p\beta^e} \right) \left( \frac{\prod_k (c_k^s)^{v_k^r\beta^e}}{\prod_k (c_k^s)^{v_k^p\beta^e}} \right) \exp \left[ \frac{\beta^e \Delta G_R^o}{RT} \right] \\
& \left( \exp \left[ \frac{(1-\beta^e)Fn\eta_s}{RT} \right] - \exp \left[ \frac{(1-\beta^e)Fn\eta_s}{RT} \right] \right)
\end{aligned} \tag{35}$$

Now the net rate of electron generation may be calculated from  $ROP_{net}$  :

$$\frac{d[e^-]}{dt} = (-n)ROP_{net} \tag{36}$$

and the current through the electrode and into the solution may be defined in terms of the electron generation rate as

$$I = F \frac{d[e^-]}{dt} \tag{37}$$

Then, the rate of progress for elementary electrode reactions may be defined in terms of the current density,  $i$ , in the traditional Butler-Volmer form as

$$i = i_o \left( \exp \left[ \frac{(1-\beta^e)F\eta_s}{RT} \right] - \exp \left[ \frac{-\beta^e F\eta_s}{RT} \right] \right) \tag{38}$$

where  $i_o$ , the exchange current density, is given by:

$$i_o = nFk_f^c \left( \prod_k^r (c_k^a)^{v_k^r(1-\beta^e)} \right) \left( \prod_k^p (c_k^a)^{v_k^p\beta^e} \right) \left( \frac{\prod_k (c_k^s)^{v_k^r\beta^e}}{\prod_k (c_k^s)^{v_k^p\beta^e}} \right) \exp \left[ \frac{\beta^e \Delta G_R^o}{RT} \right]. \tag{39}$$

Therefore, for elementary kinetics steps, Cantera's implementation leads to the Butler-Volmer format given by Eqn. (38) and (39), a point that has already been made in ref. [4]. However, for sets of interfacial electrode reactions, especially when they are intermixed with non-electrode reactions, the resulting global current density may or may not be reducible to Butler-Volmer form. A more general approach is needed.

## 6.0 Formulation of the Global Reaction Rates

There are few elementary steps in Electrode reactions that involve the transfer of more than a single electron. The hydrogen evolution reaction is not one of those. It is a combination of steps.

While each individual elementary electron-transfer reaction step obeys the Butler-Volmer, the overall reaction mechanism on a surface may not obey the Butler-Volmer formulation, Eqn. (40).

$$i_n = i_o \left( \exp \left[ \frac{\alpha_a F \eta_s}{RT} \right] - \exp \left[ \frac{-\alpha_c F \eta_s}{RT} \right] \right) \quad (40)$$

In this equation,  $i_o$  is the exchange current density and has units of A cm<sup>-2</sup>.  $i_n$  is the current density of electrons stemming from the electrode reaction.

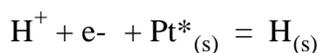
Yet, a lot of the electrochemical reaction rate data is presented in a Butler-Volmer format representing a global result. How are these issues reconciled?

They are reconciled by introducing the concept of a Global Overall Reaction, that may be defined to calculate the net rate of progress of a single reactant or product. The stoichiometry of the Global reactions are further defined via a linear combination of elementary reaction steps, such that intermediates drop out of the formulation, in order to make sure that global reactions conserve elements. However, global reaction rates are calculated using the entire reaction network and assuming intermediate quantities are at their pseudo steady-state values.

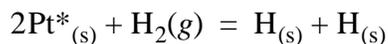
For example, below is the half-cell reaction for the standard hydrogen cell.



This may be considered to be a linear combination of two times the Volmer reaction:



added to -1 times the Tafel reaction:



Together with the specification of a special species, in this case, `Pt_electron`, the speciation allows us to calculate a specific rate of progress for the global reaction. The concept of global reaction rates has been introduced into the program `cttables`. Figure 5 contains a sample input deck for the SHE system.

For a given global reaction the product and reactant stoichiometry are uniquely specified. Therefore, the potential complication of having separate values for  $\eta_s$  defined for each elementary reaction in a complicated mechanism goes away. The equilibrium value of  $E$  is distinctly defined in terms of reaction products and reactants for that global reaction. The fact that there may be multiple pathways for getting to the products from the reactants is irrelevant to the value of  $E$ .

Newman [12] has an extensive section on the SHE kinetics. However, what's revealing is that nowhere are the rate constants or energetics of the Langmuir-Hinshelwood adsorption system that comprises the inner workings actually provided. This is true for all of the other secondary sources that I have found that discuss electrode reactions [12, 15, 16, 17, 18]. It may be, as is discussed in many of these texts, that variations due to the surface preparation of the electrode make this reaction (and many other electrode reactions) inherently irreproducible, and therefore, these sources have found it difficult to provide consistent numbers. It also may be the case that the lack of a sufficient rigorousness in the analysis, especially in earlier work before the widespread use of numerical modeling, may have hampered the derivation of the rate constants and energetics in these elementary steps.

While it may be possible to go back to the more primary literature [19] and analyze the reaction system, in putting together this sample problem, I only resorted to grossly fitting the reaction rates so that the global reaction as calculated by `cttables` fit one of Newman's Tafel plot curves for the reaction on a platinum electrode. An additional problem was that Newman's Fig. 8.6 p. 220 did not fully specify the electrolyte concentrations, which the value of the exchange current density depends on. Figure 5 specifies the composition of the solution that I used in the `cttables` calculation. The equilibrium electric potential for the reaction for this particular bath gas conditions

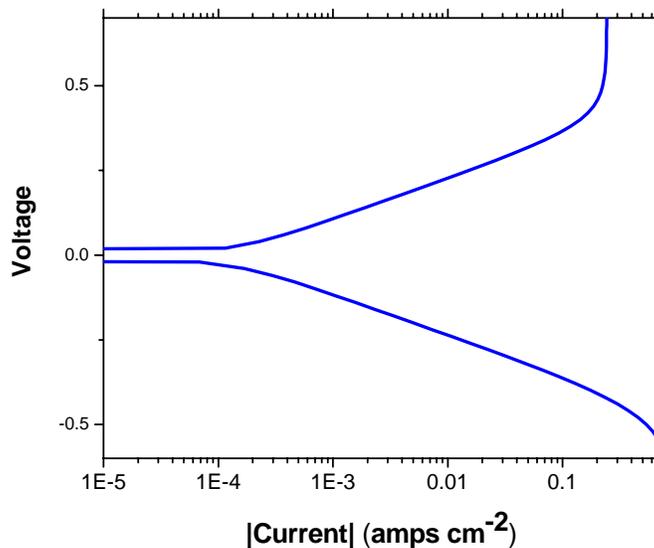
```

Number of Cantera Files = 3
Cantera File Name = Pt_electrode.xml
Cantera File Name = HMW_NaCl_sp1977_alt.xml
Cantera File Name = h2gas.xml
Bath Temperature = 300.
Bath Pressure = 1 atm
Add Chemical Potential Column = true
START BLOCK Temperature Table Format
  Number of Points = 8
  Delta Temperature = 20.
  Low Temperature = 300.
  Added Temperatures = 333.15 273.15 373.15
END BLOCK Temperature Table Format
start block Bath Specification for Phase H2gas
  Bath Species ID = H2
  start block Bath Species Mole Fraction
    H2 = 1.0
  end block Bath Species Mole Fraction
end block Bath Specification for Phase H2gas
start block Bath Specification for Phase NaCl_Electrolyte
  Bath Species ID = H2O(L)
  start block Bath Species Molalities
    Na+ = 1.0
    Cl- = 1.8
    H+ = 0.8
  end block Bath Species Molalities
end block Bath Specification for Phase NaCl_Electrolyte

Start block Extra Global Reaction
  Special Species = Pt_electron
  Start block Elementary Reaction Specification
    Reaction Index = 0
    Reaction multiplier = 2.0
  end block Elementary Reaction Specification
  Start block Elementary Reaction Specification
    Reaction Index = 1
    Reaction multiplier = -1.0
  end block Elementary Reaction Specification
End block Extra Global Reaction

```

**FIGURE 5. Sample input Deck for the `cttables` program**



**FIGURE 6. Polarization Plot for the Hydrogen electrode reaction** The current, which represents the charge flowing into the electrolyte from the electrode, is positive for voltages  $> E$  (anodic conditions) and negative for voltages  $< E$  (cathodic conditions).

turned out to be equal to  $E = -0.00494$  Volts, as the solution pH calculated from the Pitzer-based activity coefficients was 0.0839.

Over most of the curve voltages surveyed, except for extremely cathodic conditions, the surface remains dominated by free sites. This is observed in experiments. This puts a requirement on the upper bound on the heat of adsorption of hydrogen molecules on the surface. For cathodic conditions, the Tafel slope is reduced below the 0.5 limit produced by the Volmer reaction, whenever there are significant concentrations of adsorbed hydrogen; this curvature shows up a little bit in Fig. 6 at the lowest voltages. The fact the reduction in the Tafel slope is not readily seen (at least up to the voltage value of -0.6 on Pt - see p., 220 [12]) indicates, from the model, that the binding energy of Hydrogen on the surface is below a certain value. For the numbers we have used this value is 15 kJ/gmol, not a terribly high number.

Figure 6 contains the net polarization plot for the hydrogen reaction network discussed above and calculated by `cttables`. Cathodic voltages, i.e., negative voltages, produce negative values of the current, i.e., there is a net current from the electrolyte into the electrode, which in turn means that electrons are consumed at the interface. The cathodic and the anodic side of the polarization curve are not symmetric, reflecting the fact that the reaction network even for this seemingly simple reaction, is not an elementary single-step reaction. In particular, on the anodic side (high voltage where electrons are created at the interface), the reaction eventually becomes independent of the voltage. This is because the reaction becomes rate limited by adsorption rate of  $H_2(g)$  onto the bare platinum surface. In other words, the branching ratio between the reverse reaction where  $H_2(g)$  is reformed from adsorbed hydrogen and the forward step where it dissociates into  $H^+$  and an electron in the metal is skewed heavily towards the later, the electrodic reaction step.

The Butler-Volmer form of this equation is calculated by `cttables` to be equal to

$$i = 1.1157 \times 10^{-4} \left( \exp \left[ \frac{0.5F\eta_s}{RT} \right] - \exp \left[ \frac{-0.5F\eta_s}{RT} \right] \right) \quad (42)$$

At the equilibrium potential of  $E = -0.00494$  Volts, the parameters have been adjusted so that a simple Butler-Volmer (BV) form is generated at low overpotentials, as is observed in experiment. In particular the value of the BV form agrees on the cathodic side with one of Pt-metal curves in Newman's Fig. 8.6 on p.220 of ref. [12]. However, setting different parameters in the elementary reaction mechanism may lead to significantly different behavior. In particular, asymmetric Butler-Volmer behavior, where  $\alpha_a \neq \alpha_c \neq 0.5$ , may be generated when there is significant hydrogen adsorption on the Platinum.

All of this behavior can be captured by Cantera's reaction mechanism framework. However, the most important take-home point should be that the level of experimental data that is required to fully take advantage of Cantera's framework may or may not be available.

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