

Modeling Electrochemical Kinetics in Cantera

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1 Electrochemical Potential

To quantify the effect of a material's electric potential on the charge transfer rates, we can invert the equation for electric potential to get the free energy U due to the electric potential ϕ :

$$U = q\phi \quad (1)$$

the charge of a species q should be in coulombs, and can be written as Faraday's constant times the elementary charge of the ion z :

$$U = zF\phi \quad (2)$$

(for example, $z = -1$ for OH^-). This leads to the *electrochemical potential* $\tilde{\mu}$

$$\tilde{\mu} = \mu + zF\phi \quad (3)$$

The free energy driving force for an electrochemical reaction, then, is the change in electrochemical potential:

$$\Delta\tilde{G}_{\text{rxn}} = \sum \nu_k \tilde{\mu}_k = \sum \nu_k \mu_k + \sum \nu_k z_k F \phi_k \quad (4)$$

Some species k will be associated with the product potential ϕ_p , others with the reactant phase ϕ_r . Because the reaction must balance charge, the sum of the $\nu_k z_k$ must balance between the two phases (i.e. the total charge leaving one phase must enter the other). This sum can be re-labeled n , the total elementary charge transferred to the product phase:

$$\Delta\tilde{G}_{\text{rxn}} = \Delta G_{\text{rxn}} + nF\Delta\phi \quad (5)$$

where $\Delta\phi = \phi_p - \phi_r$, with p and r are the product and reactant phases. The 'product phase' must be that used to calculate n ,

$$n = \sum_p \nu_k z_k \quad (6)$$

But the designation is largely arbitrary, since the reaction can go in either direction. Consistency is all that matters - the signs of n and $\Delta\phi$ are linked. Equilibrium is reached when the total free energy of reaction $\Delta\tilde{G}_{\text{rxn}}$ equals zero, which leads to the definition of an equilibrium electric potential difference (or equilibrium voltage*) for a given state:

$$E_{\text{eq}} = V_{\text{eq}} = \Delta\phi_{\text{eq}} = \frac{-\Delta G_{\text{rxn}}}{nF} \quad (7)$$

*note that the terms "electric potential" and "voltage" are frequently used interchangeably, but "voltage" technically refers to a *difference* in electric potential.

Recall that ΔG_{rxn} is a function of conditions, such as P , T , and X_k . Each change in conditions *may* result in a different E_{eq} . There is, therefore, no single "equilibrium condition," T , P , X_k . But rather, for each T , P , X_k , there is an electric potential difference $\Delta\phi_{\text{eq}}$ which sets the reaction to equilibrium.

2 Charge Transfer Reaction Rates

2.1 Marcus Theory and Elementary Chemical Kinetics

To quantify the influence of the electrochemical potential on charge-transfer reaction rates, recall that the thermodynamic equilibrium and the kinetic equilibrium are related. For a non-electrochemical reaction, this is written as:

$$\left(\frac{k_f}{k_r}\right)^* = \exp\left(\frac{-\Delta G_{\text{rxn}}^{\circ}}{\overline{RT}}\right) [C]^{\sum \nu_k} \quad (8)$$

where * indicates the thermochemical reaction rate coefficients (i.e., in the absence of any electric potential effects. Here, all the standard relationships between thermo properties and Arrhenius parameters still apply, even for charge-transfer reactions). ν_k is the *net* stoichiometric coefficient of species k and $[C]$ is the total concentration (note that $[C]$ is probably not sufficiently generalized, but doesn't really matter, for our purposes). For the charge-transfer reaction, thermodynamic equilibrium is written as:

$$\Delta \tilde{G}_{\text{rxn}} = \Delta G_{\text{rxn}} + nF\Delta\phi = \Delta G_{\text{rxn}}^{\circ} + \overline{RT} \ln\left(\prod X_k^{\nu_k}\right) + nF\Delta\phi \quad (9)$$

as with thermal kinetics, we can calculate a kinetic equilibrium coefficient by isolating $\prod X_k^{\nu_k}$ (again, note that the use of X_k assumes a certain thermodynamic model and can be generalized further, but will suffice for our example):

$$\frac{k_f}{k_r} = \exp\left(\frac{-\Delta G_{\text{rxn}}^{\circ}}{\overline{RT}}\right) \exp\left(\frac{-nF\Delta\phi}{\overline{RT}}\right) [C]^{\sum \nu_k} = \left(\frac{k_f}{k_r}\right)^* \exp\left(\frac{-nF\Delta\phi}{\overline{RT}}\right) \quad (10)$$

where $\left(\frac{k_f}{k_r}\right)^*$ is the ratio of the kinetic rate parameters for the non-electrochemical reaction. So we know that the voltage difference affects the free energy of reaction, which shifts the *ratio* of the rates for a charge-transfer reaction by $\exp\left(\frac{-nF\Delta\phi}{\overline{RT}}\right)$, but not how this specifically effects the forward or reverse rates.

For this, we must realize that some fraction β_f of the free energy change will affect the forward reaction, while a fraction β_r will affect the reverse reaction. For an elementary charge-transfer reaction, we must have $\beta_f + \beta_r = 1$. For this case, letting $\beta \equiv \beta_f$, we get:

$$\frac{k_f}{k_r} = \left(\frac{k_f}{k_r}\right)^* \frac{\exp\left(\frac{-\beta nF\Delta\phi}{\overline{RT}}\right)}{\exp\left(\frac{(1-\beta)nF\Delta\phi}{\overline{RT}}\right)} \quad (11)$$

and therefore:

$$k_f = k_f^* \exp\left(\frac{-\beta nF\Delta\phi}{\overline{RT}}\right) \quad (12)$$

$$k_r = k_r^* \exp\left(\frac{(1-\beta)nF\Delta\phi}{\overline{RT}}\right) \quad (13)$$

pay careful attention to signs: recall that n here is the total *charge number* transferred. If the net reaction moves one electron from a phase at ϕ_r to a phase at ϕ_p , then $n = -1$.

The rate of progress for a charge transfer reaction i is therefore:

$$\dot{q}_i = k_f^* \prod [X_k]^{\nu'_k} \exp\left(\frac{-\beta nF\Delta\phi}{RT}\right) - k_r^* \prod [X_k]^{\nu''_k} \exp\left(\frac{(1-\beta)nF\Delta\phi}{RT}\right) \quad (14)$$

The k_f^* and k_r^* are the standard chemical reaction rate coefficients, calculated according to Arrhenius parameters or some other formulation.

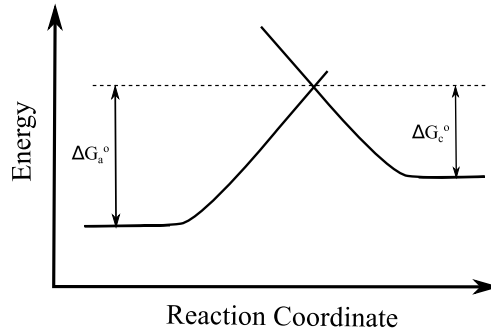
The current density i can be written as:

$$i = nF\dot{q} \quad (15)$$

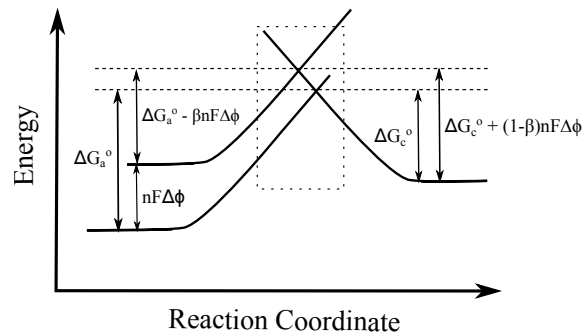
Note that kinetic and thermodynamic equilibrium are reached when $\Delta\phi = E_{\text{eq}}$, from eq. 7, above. So when $\Delta\phi = E_{\text{eq}}$, then $i = 0$.

2.2 Another Perspective: Free Energy Diagrams

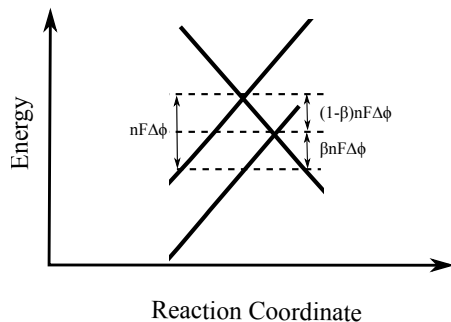
But what is β ? To determine the physical nature of the *charge transfer coefficient* β , we turn to transition state theory. For the chemical reaction with no electric potential difference, there is a free energy barrier ΔG° in both the anodic (ΔG_a°) and cathodic (ΔG_c°) directions.



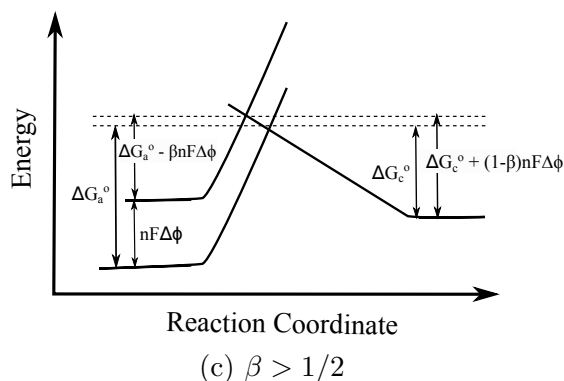
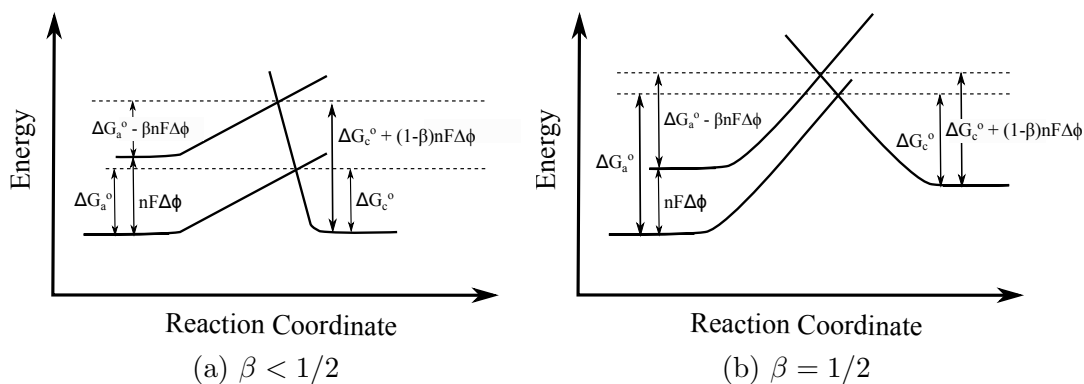
If we apply an electric potential across the interface, the change in free energy ($nF\Delta\phi$) affects the barrier in both the forward and reverse directions:



Zooming in on the dashed box:



we see that the transition state free energy increases by a fraction $(1 - \beta)$ of the total shift $nF\Delta\phi$. The *height* of the forward barrier, therefore, decreases by $nF(\Delta\phi - (1 - \beta)\Delta\phi) = \beta nF\Delta\phi$. Similarly, the reverse barrier increases by $(1 - \beta)nF\Delta\phi$. The fraction β is determined by the slope of the energy surface for the forward and reverse directions:



This provides another pathway to understanding the exponential terms applied to the forward and reverse rates in eq. 14. Rates are adjusted by $\exp\left(-\frac{\Delta E_a}{RT}\right)$, where ΔE_a is the change in the barrier height ($-\beta nF\Delta\phi$ for the forward reaction, and $(1 - \beta)nF\Delta\phi$ for the reverse reaction). Note that we could derive eq. 14 entirely from transition state theory, if we desired.

2.3 The Butler-Volmer Formulation

While our charge-transfer reaction rate in eq. 14 has a simple physical origin in state variables, it can be computationally unwieldy. For a simpler representation, the reaction rate is more commonly written in *Butler-Volmer* (B-V) form:

$$i = i_o \left[\exp\left(\frac{\alpha_f n F \eta}{RT}\right) - \exp\left(-\frac{\alpha_r n F \eta}{RT}\right) \right] \quad (16)$$

where $\eta = E - E_{\text{eq}}$ (or $\Delta\phi - \Delta\phi_{\text{eq}}$) is the *overpotential*—the electric potential driving force for the reaction in the forward direction, relative to the chemical potential driving force.

The variable i_o is known as the *exchange current density*. At equilibrium, while the net rate is zero, there is progress in both the forward and reverse reactions, just at equal rates. The exchange current density *is* this rate of one-way reactions at equilibrium. For reactions moving back and forth at a fast rate, a little “nudge” by the electric potential can lead to a fast rate of reaction (i.e., high current). For a low exchange current density, it takes a larger driving force – a larger overpotential η – to reach high currents.

The α values correspond loosely to the β parameters in eq. 14, but the Butler-Volmer formulation is often applied for non-elementary reactions, in which $\alpha_f + \alpha_r = 1$ is not necessarily true.* However, assuming $\beta = \alpha_f$ and $1 - \beta = \alpha_r$, the current density given by eqs. 14 - 15 can be converted to eq. 16, with:

$$i_o = n F k_f^{*(1-\beta)} k_r^{*\beta} \prod [X_k]^{(1-\beta)\nu'_k} \prod [X_k]^{\beta\nu''_k}, \quad (17)$$

where ν'_k and ν''_k are the forward and reverse stoichiometric coefficients, respectively, and where $[X_k]$ represents the generalized ‘activity concentraion’ used in Cantera.

*Note that the B-V equation for global reactions is only true/appropriate if there is a *single rate-determining step* in the global mechanism. Otherwise the entire idea of a $\Delta\phi_{\text{eq}}$ and therefore the calculation of η is a source of great ambiguity.

2.4 Butler-Volmer “Flavors”

There are a few common variants to how B-V is typically implemented:

2.4.1 The Tafel Equation

For larger currents or large overpotentials η , the reverse rate (the second exponential in eq. 16) rapidly approaches zero, and eq. 16 reduces to:

$$i = i_o \exp\left(\frac{\beta n F \Delta\phi}{RT}\right) \quad (18)$$

This form cannot produce equilibrium (i.e. $i \rightarrow 0$ only as $\eta \rightarrow -\infty$), but is a commonly-used analytical form to recover i_o and α_f/α_r from experimental data.

2.4.2 Constant i_o

Note that this is patently incorrect— i_o is a function of local conditions—but may be moderately appropriate within certain operating regimes (very low fuel utilization, constant local composition, etc.). It is, therefore, not uncommon in electrochemical literature.

2.4.3 User-specified Reactant Orders

Some users may want to specify reactant orders for the exchange current density:

$$i_o = nFk_f^{*(1-\beta)}k_r^{*\beta} \prod [X_k]^{n_{k,\text{fwd}}} \prod [X_k]^{n_{k,\text{rev}}}, \quad (19)$$

where the orders $n_{k,\text{fwd}}$ and $n_{k,\text{rev}}$ replace $(1-\beta)\nu'_k$ and $\beta\nu''_k$ in eq. 19, respectively. Note that this works in the B-V form, only, and not in the Marcus theory form, because the net production rate for a species k from this reaction is:

$$\dot{s}_{k,\text{BV}} = \nu_k q_{\text{BV}} = \nu_k \frac{i}{nF} \quad (20)$$

and thermodynamic consistency is maintained, as η is evaluated relative to:

$$\Delta\phi_{\text{rev}} = -\frac{\Delta G_{\text{rxn}}}{nF} = -\frac{\sum \nu_k \mu_k}{nF}. \quad (21)$$

with the actual ν_k used in eqs. 20 and 21, not the user-specified orders n_k .

2.4.4 User-specified Species Dependency Functions

Disclosure: this is a longer-term “wouldn’t it be nice” goal, with a murky implementation.

Anyway: for mechanisms with a single rate-limiting step, assuming partial equilibrium for all non-rate-limiting steps eliminates those reactions from the mechanism. One replaces the concentration dependencies of intermediate species in eq. 19 with equilibrium expressions. For one example, see eqs. 37–47 in Zhu, Kee, et al., *J. Electrochem. Soc.*, 2005 (linked [here](#)). In that paper, eqs. 16 and 19 for a simple H₂ oxidation reaction reduce to:

$$i = i_o \left[\exp\left(\frac{(\beta_{\text{RL}} + 1) F \eta}{RT}\right) - \exp\left(-\frac{\beta_{\text{RL}} F \eta}{RT}\right) \right], \quad (22)$$

and

$$i_o = i_o^* \frac{(p_{\text{H}_2}/p_{\text{H}_2}^*)^{1/4} (p_{\text{H}_2\text{O}})^{3/4}}{1 + (p_{\text{H}_2}/p_{\text{H}_2}^*)^{1/2}}. \quad (23)$$

Here, β_{RL} refers to the symmetry factor for the rate-limiting step and i_o^* is the exchange current density at a reference condition * (where species partial pressures are p_k^*).

Enabling partial-equilibrium functionality spares users from specifying/fitting unknown rate constants for the equilibrated steps and reduces mechanism size. Functionally, a user could write the full mechanism and just specify really fast rates for the equilibrated steps, but a) this adds reactions to the mech that are not entirely necessary, and b) there can be stiffness issues, if the rate chosen is *too* fast. That said, (i) the functional forms can be quite complex, (ii) how we enable an interface for specifying them is not entirely clear, and (iii) the number of users with the knowledge and interest in this functionality might be rather limited, at present. But it may one day be relevant/useful, so I thought I’d just plant a seed, in case anyone has an idea.

3 Cantera Implementation

Here is the functionality I think we should enable in Cantera.

For all reactions, I think the user should be able to query the current density (both for individual reactions and summing over all reactions for a given interface).

For specific reaction types (Marcus theory vs. Butler–Volmer):

3.1 Marcus Theory

3.1.1 User Inputs

For the ‘standard’ treatment described in sec. 2.1, things operate largely as they should. Users should be able to:

- Pass in a k_{fwd}
- Pass in i_o and have it converted to an equivalent k_{fwd}

3.1.2 Detection

We currently provide the following means of indicating an electrochemical reaction:

- Specify a β value
- Provide an i_o value.
- In the absence of either of these, the reaction string is parsed to automatically detect a charge-transfer reaction.
- I. Schoegl has suggested that we add some type of flag.

It think this is a good idea, but should be optional, on the user end. Correctly evaluating the reaction driving forces is not a ‘special feature’ that a user needs to request, imho.

But the larger question of when to parse the equation strings and when/how to mark an ‘electrochemical’ reaction is worth evaluating. At present we parse all surface reaction equation strings twice. Can we shift the labeling of echem reactions in some way such that this designation is made during the ‘main’ reaction string parsing? It would be nice.

- Another thought: I’ve got half a mind that we can derive a method to fold electric potential effects directly into the species activities, such that electrochemical reactions don’t require any special handling.

Here, electric potential effects would be part of the activity calculation, where this impact evaluates to multiplication by 1.0 for non-charge-transfer reactions. This requires a little more thought, as it has both theoretical and implementation hurdles. But it is worth exploring.

3.2 Butler–Volmer

First, given what I’m about to propose below, I do think that Butler–Volmer needs to be its own, separate reaction type. While the main equation (eq. 16) can be converted back to Marcus Theory, there are enough variants that justify special handling. This also eliminates any need for detection of charge transfer.

3.2.1 User Inputs

The user should be able to:

- Pass in a k_{fwd} and have it converted to an equivalent i_o .
- Pass in i_o (likely via Arrhenius parameters).
- Pass in i_o^* for a known reference state (known species concentrations), along with a list of these reference concentrations $[X_k^*]$. The expression for i_o then becomes:

$$i_o = i_o^* \prod \left(\frac{[X_k]}{[X_k^*]} \right)^{(1-\beta)\nu_k'} \prod \left(\frac{[X_k]}{[X_k^*]} \right)^{\beta\nu_k''} \quad (24)$$

- Pass in non-stoichiometric species orders for i_o .
- An ‘options’ flag that allows the user to specify use of the Tafel equation (eq. 18).

3.2.2 Outputs

The user should also be able to query, for a given state:

- The exchange current density i_o
- The overpotential $\eta = \Delta\phi - \Delta\phi_{\text{eq}}$.