

**ME 370B**  
**Energy Systems II:**  
**Modeling and Advanced Concepts**

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**An Alternative Approach to Reaction Rates for Fuel Cells**

Transition-state theory provides a linkage between the reaction rate and transition-state Gibbs function for reactants at the standard concentration and level of activity.<sup>1</sup>

The standard-state forward rate constant can be expressed in terms of the amount by which the Gibbs function of the transition state exceeds that of the standard reference state of the collective reactants (see Levine, p. 905)

$$k_f = \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_R^\circ)}{\bar{R}T} \right]$$

What this says physically, is that the rate at which the reactants pass through the transition state (and become products) is given by the product of a thermal attempt frequency  $k_B T/h$  and the (Boltzmann) probability that the reactants have, at the standard state, a collective Gibbs function,  $G_R^\circ = \sum_{R,i} \nu_i \mu_i^\circ$ , that exceeds the threshold value for the transition state  $G^\ddagger$ . Note that for this

expression to be valid, the conditions under which the standard-state chemical potentials are defined must remain fixed. Since the chemical potential of species  $i$  in solvent  $A$  (or on a surface site  $A$ ), but in the presence of other reactant species  $j \neq i, A$ , may be written in the general form

$$\mu_i(T, P, a_i, a_A, \{a_{j \neq i, A}\}) = \mu_i^\circ(T, P, a_i^\circ, a_A^\circ, \{a_{j \neq i, A} = 0\}) + \bar{R}T \ln(a_i/a_i^\circ)$$

where  $\mu_i^\circ(T, P, a_i^\circ, a_A^\circ, \{a_{j \neq i, A} = 0\})$  is the chemical potential in the absence of the other reactants,  $a_A^\circ$  is the activity of the solvent (which may have a non-unity activity coefficient at the standard state due to the presence of species  $i$  altering its pure-fluid structure), and  $a_i/a_i^\circ$  is the ratio of activity coefficients of the species between actual conditions and the reference condition when it is the only reactant present (in the solvent or on the site).<sup>2</sup>

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<sup>1</sup> The “concentration” may be per unit volume (number density), per unit area (surface density), or even per unit length (e.g., sites per unit length on a catalytic wire). The “level of activity” recognizes the fact that if the reactants are present in a solvent or at a surface site, their chemical potential is likely to be affected such that it will not be identical with that of the pure substance at the same concentration.

<sup>2</sup> Note that it is also possible to have the situation where both a solvent and surface sites must be considered in addition to the “reactant” species (e.g., in supercritical-solvent, slurry reactors for Fischer-Tropsch synthesis). Although this does not change the essence of the analysis presented here, it does further complicate the already-overcomplicated notation such that we will not attempt to include it in this discussion. Hopefully the extensions required to treat this case are suggested by the solvent/surface discussion included here already.

The actual reaction rate differs from this standard-state rate by virtue of the concentration and activity of the actual reactants. Written in terms of the activity of the reactants, the forward reaction rate may be written as (see Levine p. 560)

$$R_f = k_f Y \prod_{R,i} (a_i/a_i^o)^{v_i} = \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_R^o)}{\bar{R}T} \right] Y \prod_{R,i} (a_i/a_i^o)^{v_i}$$

where  $Y = (a^\ddagger/a^{o\ddagger})^{-1} = 1/\gamma^\ddagger = Y(T, P, \text{solvent or site})$  is the inverse of the activity coefficient of the activated complex of the reaction at the transition state (see Levine p. 909).

The product term can be written as

$$\prod_{R,i} (a_i/a_i^o)^{v_i} = \exp \left[ \ln \prod_{R,i} (a_i/a_i^o)^{v_i} \right] = \exp \left[ \sum_{R,i} \ln (a_i/a_i^o)^{v_i} \right]$$

such that the expression for the reaction rate becomes

$$R_f = Y \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_R^o)}{\bar{R}T} + \sum_{R,i} \ln (a_i/a_i^o)^{v_i} \right]$$

Since  $G_R^o = \sum_{R,i} v_i \mu_i^o$  this can be written as

$$\begin{aligned} R_f &= Y \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-1}{\bar{R}T} \left( G^\ddagger - \sum_{R,i} \left[ v_i \mu_i^o + \bar{R}T \ln (a_i/a_i^o)^{v_i} \right] \right) \right] \\ &= Y \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-1}{\bar{R}T} \left( G^\ddagger - \sum_{R,i} v_i \left[ \mu_i^o + \bar{R}T \ln (a_i/a_i^o) \right] \right) \right] \end{aligned}$$

But, by definition,  $G_R = \sum_{R,i} v_i \mu_i = \sum_{R,i} v_i \left[ \mu_i^o + \bar{R}T \ln (a_i/a_i^o) \right]$ , such that the reaction rate may be written directly in terms of the collective Gibbs function of the reactants as

$$R_f = \frac{1}{\gamma^\ddagger} \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_R)}{\bar{R}T} \right]$$

This expresses the not-too-surprising fact that the overall reaction rate depends on the probability that the *actual* Gibbs function of the reactants exceeds the threshold of the transition state. Note that if the transition-state Gibbs function is defined with respect to the actual surface or solvent conditions under which the transition state Gibbs function is obtained (either by quantum calculations or experiment), its activity coefficient  $\gamma^\ddagger$  will be unity, having been necessarily incorporated into the conditions that define the transition state.

In the same fashion, the backward rate of the reaction may be written directly in terms of the Gibbs function of the products as

$$R_b = \frac{1}{\gamma^\ddagger} \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_p)}{\bar{R}T} \right]$$

These expressions must hold under all conditions, including equilibrium. At equilibrium, the reaction rate (that is, the *exchange* reaction rate) can be written based on the forward rate as

$$R_{eq} = R_{f,eq} = k_f \frac{1}{\gamma_{eq}^\ddagger} \prod_{R,i} (a_{i,eq} / a_i^o)^{\nu_i} = \frac{1}{\gamma_{eq}^\ddagger} \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_{R,eq})}{\bar{R}T} \right]$$

The ratio of the forward reaction rate under any condition to the equilibrium (exchange) rate is then

$$\frac{R_f}{R_{eq}} = \frac{\gamma_{eq}^\ddagger}{\gamma^\ddagger} \exp \left[ \frac{-(G^\ddagger - G_R)}{\bar{R}T} - \frac{-(G^\ddagger - G_{R,eq})}{\bar{R}T} \right] = \frac{\gamma_{eq}^\ddagger}{\gamma^\ddagger} \exp \left( \frac{G_R - G_{R,eq}}{\bar{R}T} \right)$$

If the equilibrium rate is known, the rate at any non-equilibrium condition can be written in terms of the equilibrium rate as

$$R_f = R_{eq} \frac{\gamma_{eq}^\ddagger}{\gamma^\ddagger} \exp \left( \frac{G_R - G_{R,eq}}{\bar{R}T} \right)$$

What we have done, in effect, is to use the empirical knowledge supplied by the equilibrium exchange rate to eliminate the need to know the transition state Gibbs function explicitly.

Following the same logic, the reverse rate can be written as

$$R_b = R_{eq} \frac{\gamma_{eq}^\ddagger}{\gamma^\ddagger} \exp \left( \frac{G_P - G_{P,eq}}{\bar{R}T} \right)$$

The net forward reaction rate (the *reaction velocity*<sup>3</sup>) can now be written in terms of the actual Gibbs functions of the reactants and products and their equilibrium values (corresponding to the exchange reaction rate) as

$$v = R_f - R_b = R_{eq} \frac{\gamma_{eq}^\ddagger}{\gamma^\ddagger} \left[ \exp \left( \frac{G_R - G_{R,eq}}{\bar{R}T} \right) - \exp \left( \frac{G_P - G_{P,eq}}{\bar{R}T} \right) \right]$$

Since the environment ( $T$ ,  $P$ , and solvent or surface site) in which the reaction takes place must remain unchanged between the equilibrium state and the nonequilibrium state for the transition

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<sup>3</sup> The name reaction velocity will seem odd to most engineers since this involves neither a rate of motion in physical space nor is it a vector quantity. It comes from chemistry and it is simply the net reaction rate—how many times the reaction it describes is executed per unit volume or area or whatever spatial parameter is used to describe the equilibrium exchange rate. (E.g.: For a fuel cell, this will be reactions per unit area of the membrane per unit time.)

state to remain unchanged, then it follows that the activity coefficient of the transition state complex also remains unchanged and the activity ratio is unity. This yields the expression

$$v = R_f - R_b = R_{eq} \left[ \exp \left( \frac{G_R - G_{R,eq}}{\bar{R}T} \right) - \exp \left( \frac{G_P - G_{P,eq}}{\bar{R}T} \right) \right]$$

Note that if the reaction is electrochemical in nature, the Gibbs function of the reactants must include the electrical component as well, such that this becomes

$$v = R_f - R_b = R_{eq} \left[ \exp \left( \frac{\tilde{G}_R - \tilde{G}_{R,eq}}{\bar{R}T} \right) - \exp \left( \frac{\tilde{G}_P - \tilde{G}_{P,eq}}{\bar{R}T} \right) \right]$$

with  $\tilde{G}_R \equiv \sum_{R,i} \nu_i \tilde{\mu}_i = \sum_{R,i} \nu_i \left[ \tilde{\mu}_i^o(T, P, a_i^o, a_A^o, \{a_{j \neq i, A} = 0\}, \phi^o) + \bar{R}T \ln(a_i/a_i^o) + z_i F(\phi - \phi^o) \right]$  and  $\tilde{G}_P \equiv \sum_{P,i} \nu_i \tilde{\mu}_i = \sum_{P,i} \nu_i \left[ \tilde{\mu}_i^o(T, P, a_i^o, a_A^o, \{a_{j \neq i, A} = 0\}, \phi^o) + \bar{R}T \ln(a_i/a_i^o) + z_i F(\phi - \phi^o) \right]$ .

### Specialization for the Problem of Gas/Surface Reaction

In the case of surface reaction of species supplied by, and removed to, an adjacent gas phase, it is common to consider the site independently from the list of reactants and to include it separately and explicitly (i.e., not as species A above). This allows attention to be focused on the mobile species that can be affected by changes taking place elsewhere in the system.

Denoting the area density of independent reaction sites by  $n_s$ , the chemical potential may be written as

$$\mu_i(T, P, a_i, n_s = 1, \{a_{j \neq i, A}\}) = \mu_i^o(T, P, a_i^o, n_s = 1, \{a_{j \neq i, A} = 0\}) + \bar{R}T \ln(a_i/a_i^o)$$

where  $\mu_i^o(T, P, a_i^o, n_s = 1, \{a_{j \neq i, A} = 0\})$  is the chemical potential of the species at an independent site in the absence of the other reactants, and  $a_i/a_i^o$  is the ratio of activity coefficients of the species between the actual conditions and the reference condition when it is the only reactant present at the site.

The forward reaction rate can then be written explicitly in terms of the site density as

$$R_f = k_f n_s Y_s \prod_{R,i} (a_i/a_i^o)^{\nu_i} = n_s Y_s \left( \frac{k_B T}{h} \right) \exp \left[ -\frac{(G^\ddagger - G_R^o)}{\bar{R}T} \right] \prod_{R,i} (a_i/a_i^o)^{\nu_i}$$

where  $Y_s = Y_s(T, P, \text{site}) = 1/\gamma_s^\ddagger$  is the inverse of the activity coefficient of the activated complex of the reaction at the site.

Following the same line of logic as for the general case, this may be manipulated to yield

$$R_f = \frac{n_s}{\gamma_s^\ddagger} \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_R)}{\bar{R}T} \right]$$

and similarly

$$R_b = \frac{n_s}{\gamma_s^\ddagger} \left( \frac{k_B T}{h} \right) \exp \left[ \frac{-(G^\ddagger - G_P)}{\bar{R}T} \right]$$

Once the exchange rate has been used to eliminate the transition-state Gibbs function, both the explicit dependence on site density and on activity disappear (are subsumed into the exchange rate), and the remainder of the analysis, including the electrochemical extension, is unaltered.

$$R_f = R_{eq} \exp \left( \frac{G_R - G_{R,eq}}{\bar{R}T} \right), \quad R_b = R_{eq} \exp \left( \frac{G_P - G_{P,eq}}{\bar{R}T} \right)$$

$$v = R_f - R_b = R_{eq} \left[ \exp \left( \frac{\tilde{G}_R - \tilde{G}_{R,eq}}{\bar{R}T} \right) - \exp \left( \frac{\tilde{G}_P - \tilde{G}_{P,eq}}{\bar{R}T} \right) \right]$$

Note that the existence of a “site” is intimately tied to the value of the transition state Gibbs function. Since it is assumed that there is only one kind of site, there is only one barrier height to be surmounted. In practice, the activity of surface sites varies according to both structure (edge, kink, etc.) and temperature, such that sites that were once inactive may become active under certain conditions (and vice versa). As such, the treatment here—considering only a fixed density of sites, (albeit with a temperature-dependent transition state Gibbs function), is oversimplified.