

Lecture 8

Electron Transfer Reactions at Metal Electrodes

Outer and Inner Sphere Electron Transfer Processes

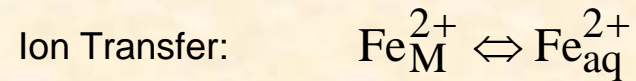
Butler-Volmer equation

Transition State Theory - A Semi-Quantitative Approach

The Gerischer's Formulation

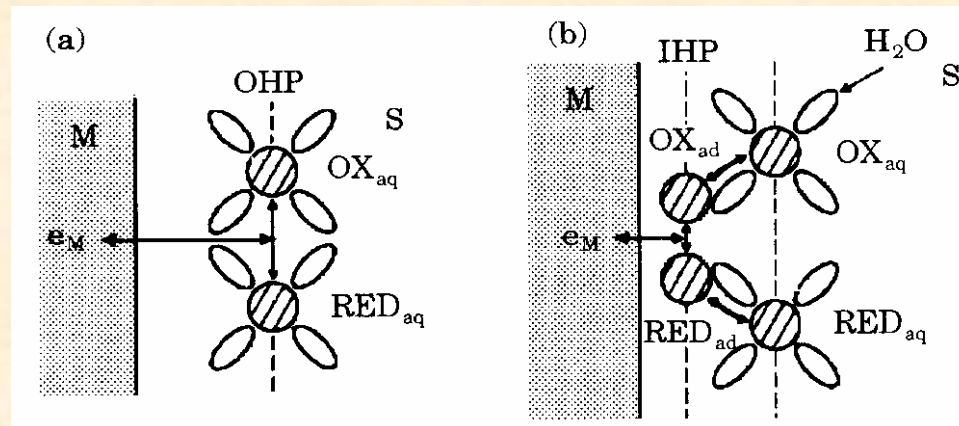
Faradaic Reactions at Metal Electrodes

Electrode reactions can be divided into two general groups



As we have discussed many times, electrons are Fermions while ions follow the Boltzmann statistic. Consequently, the physical aspects behind these processes are entirely different.

Here, we shall concentrate on *Electron Transfer at metallic electrodes*.



Outer sphere reactions involves the tunnelling of electrons across the compact layer. Roughly independent of the electrode properties.

Inner sphere reactions involves dehydrated redox particles at the IHP (adsorbed species)

Phenomenological Relationship Between Current and Electrode Potential

The rate of electron transfer can be simply described as in homogeneous chemical kinetics

$$v = k_{\text{ox}} c_{\text{red}}^{\text{s}} - k_{\text{red}} c_{\text{ox}}^{\text{s}} \quad 8.1 \quad \text{where from the absolute rate theory it follows,}$$

$$k_{\text{ox}} = A \exp\left(-\frac{\Delta G_{\text{ox}}^*(\phi)}{kT}\right) \quad 8.2 \quad \text{activation energy} \quad k_{\text{red}} = A \exp\left(-\frac{\Delta G_{\text{red}}^*(\phi)}{kT}\right) \quad 8.3$$

The activation terms are dependent on the electrode potential but not the pre-exponential factor.

$$\Delta G_{\text{ox}}^*(\phi) = \Delta G_{\text{ox}}^*(\phi_{\text{eq}}^{\circ}) - \alpha e(\phi - \phi_{\text{eq}}^{\circ}) \quad \alpha = -\frac{1}{e} \left. \frac{\partial \Delta G_{\text{ox}}^*(\phi)}{\partial \phi} \right|_{\phi_{\text{eq}}^{\circ}} \quad 8.4$$

$$\Delta G_{\text{red}}^*(\phi) = \Delta G_{\text{red}}^*(\phi_{\text{eq}}^{\circ}) + \beta e(\phi - \phi_{\text{eq}}^{\circ}) \quad \beta = \frac{1}{e} \left. \frac{\partial \Delta G_{\text{red}}^*(\phi)}{\partial \phi} \right|_{\phi_{\text{eq}}^{\circ}} \quad 8.5$$

It follows that the Gibbs energy of activation and reaction are correlated by:

$$\Delta G_{\text{ox}}^* (\phi) - \Delta G_{\text{red}}^* (\phi) = G_{\text{ox}} - G_{\text{red}} \quad 8.6a \quad \Delta G_{\text{ox}}^* (\phi_{\text{eq}}^\circ) = \Delta G_{\text{red}}^* (\phi_{\text{eq}}^\circ) = \Delta G_{\text{eq}}^* \quad 8.6b$$

Assuming an outer sphere electron transfer reaction in which the electrostatic energy of the ionic species is not significantly affected by the electrode potential, it follows that

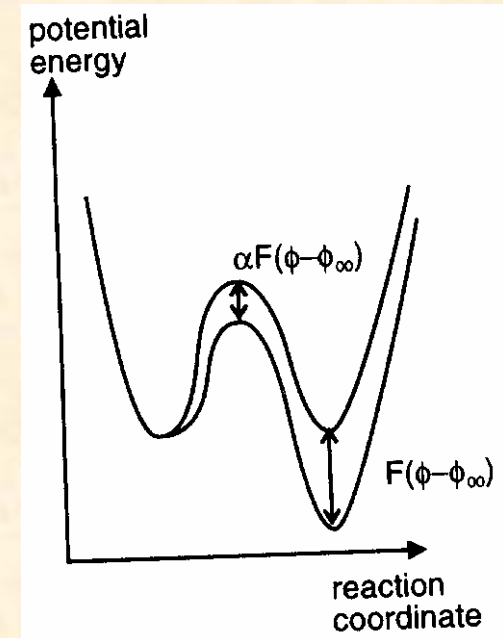
$$\Delta G_{\text{ox}}^* (\phi) - \Delta G_{\text{red}}^* (\phi) = -e(\phi - \phi_{\text{eq}}^\circ) \quad 8.7$$

Differentiating eqs. 8.4, 8.5 and 8.7, we obtain $\alpha + \beta = 1$ 8.8

Further developing eq. 8.1, we get

$$J = ek_0 c_{\text{red}}^s \exp\left[\frac{\alpha e(\phi - \phi_{\text{eq}}^\circ)}{kT}\right] - ek_0 c_{\text{ox}}^s \exp\left[-\frac{(1-\alpha)e(\phi - \phi_{\text{eq}}^\circ)}{kT}\right] \quad 8.9$$

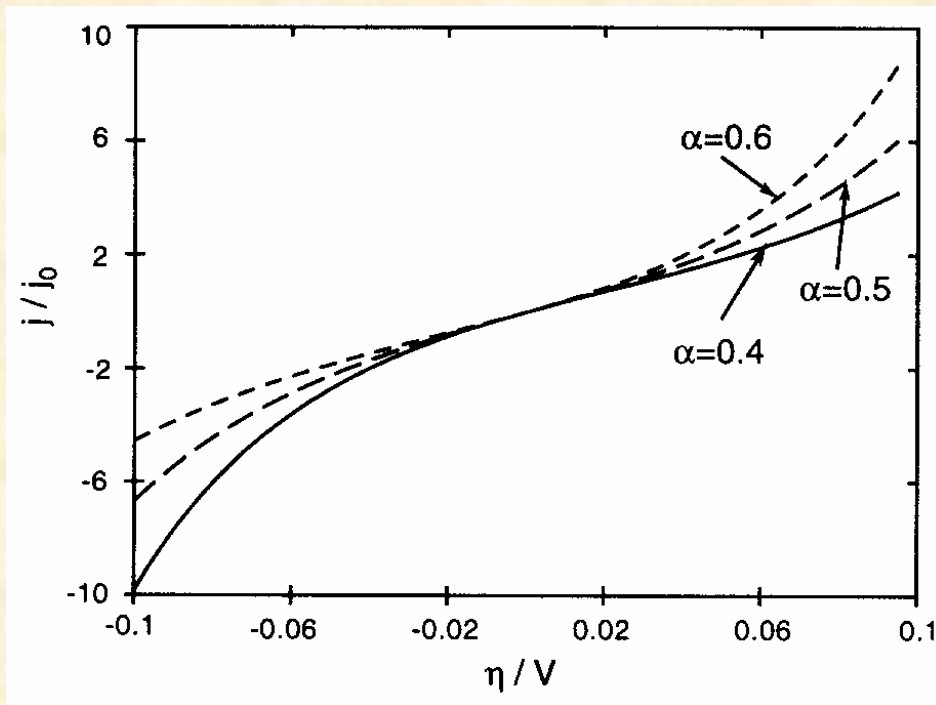
where $k_0 = A \exp\left(-\frac{\Delta G_{\text{eq}}^*}{kT}\right)$ 8.10



Recalling the Nernst equation (5.21),
$$\phi_{\text{eq}} = \phi_{\text{eq}}^{\circ} + \frac{kT}{e} \ln \left(\frac{c_{\text{ox}}^{\text{s}}}{c_{\text{red}}^{\text{s}}} \right) \quad 8.11$$

We can finally derive the Butler-Volmer equation for electron transfer reactions

$$J = J_{\circ} \left[\exp \left(\frac{\alpha e \eta}{kT} \right) - \exp \left(-\frac{(1-\alpha) e \eta}{kT} \right) \right] \quad 8.12$$



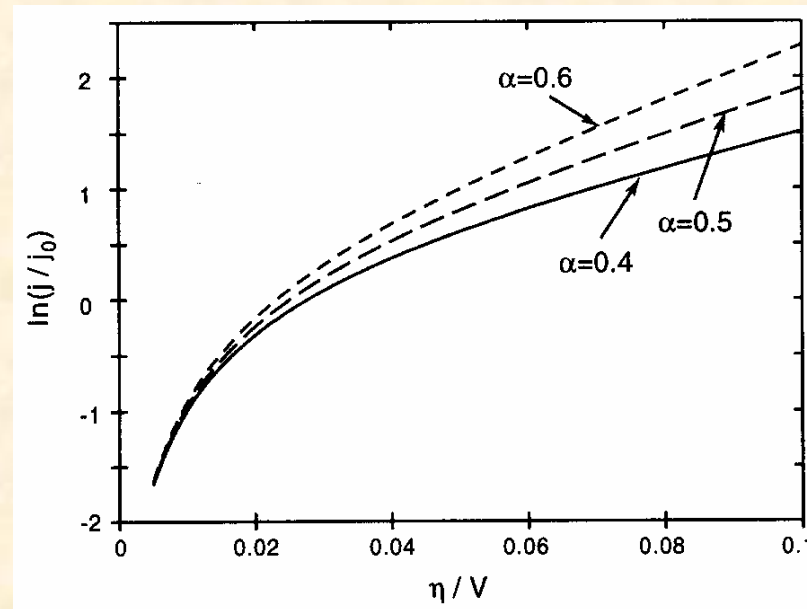
$$J_{\circ} = e k_{\circ} (c_{\text{red}}^{\text{s}})^{1-\alpha} (c_{\text{ox}}^{\text{s}})^{\alpha}$$

Exchange current density

$$\eta = (\phi - \phi_{\text{eq}})$$

Overpotential

For large overpotentials: logarithmic dependence of the current density with the overpotential (*Tafel regime*).



For low overpotentials: the system behave linearly as an ohmic resistance $J = J_0 \frac{e\eta}{kT}$

Few further remarks: the transfer coefficient α is equivalent to the Broenstedt coefficient.

α determines the symmetry (or lack of) of the current potential curve.

The Butler-Volmer analysis based on surface concentrations.

Forget expression 8.12 for inner sphere reactions.

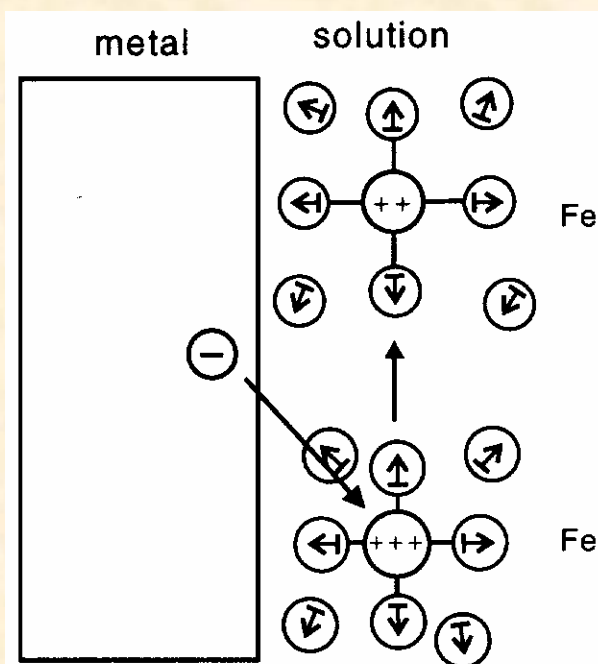
A Semi-quantitative Approach to Electron Transfer Rate Constant

Qualitatively, we can visualise outer sphere electron transfer in a series of steps involving the approach of reactants to the electrode surface, reorganisation of the solvent structure and electron tunnelling. For these reasons, although outer sphere reactions are fast indeed, they are not infinitely fast! Typical activation energies lie around 0.2 to 0.4 eV.

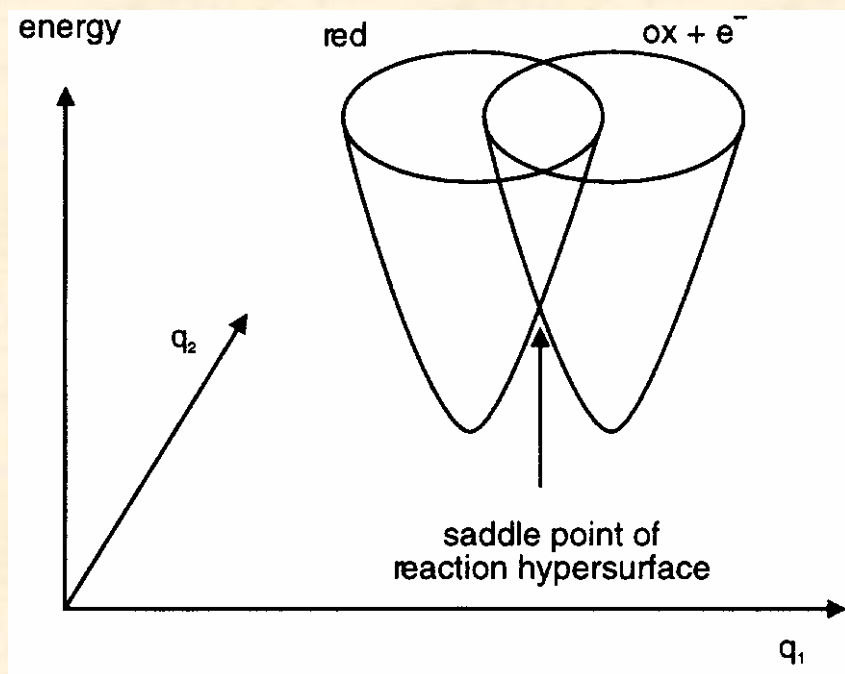
Frank-Condon

principle:

- 1.- Heavy particles of the inner and outer sphere must assume a suitable intermediate configuration
- 2.- Electron exchange is isoenergetic.
- 3.- System relax to its new equilibrium configuration



This chain of events can also be rationalised in terms of *potential energy surface diagrams*,



The reaction will take place via the Saddle point of the intersection between the two hypersurfaces. At this point, the activation energy is minimised. If the electron transfer takes place as soon as the system reach the Saddle point, then the reaction is considered adiabatic. If the system passes several times through this point with no electron transfer, the process is referred to as Non-adiabatic.

For a more quantitative approach to the electron transfer rate, we need to tackle the contributions of the inner and outer sphere as well as their reorganisation. Let us use the *harmonic approximation*. Around equilibrium, the potential energy of the system is developed into a power series of the various coordinates involved. The series is taken up to the second term (this is why we draw parabolas and paraboloids). By choosing the appropriate set of coordinates, we can eliminate the cross-terms between the various coordinates, leaving a set of independents oscillators (intersection of paraboloids).

For electron transfer, we must define the coordinates for each of the oxidised states (q_i) with respect to the equilibrium positions (y_i):

$$U_{\text{ox}}(q_i) = e_{\text{ox}} + \sum \frac{1}{2} m_i \omega_i^2 (q_i - Y_{i,\text{ox}})^2$$

8.13

e_i are the potential energy
at equilibrium

$$U_{\text{red}}(q_i) = e_{\text{red}} + \sum \frac{1}{2} m_i \omega_i^2 (q_i - Y_{i,\text{red}})^2$$

8.14

m_i and ω_i are the effective mass and
frequency of mode i , respectively

As a first approximation $\omega_{i,\text{ox}} = \omega_{i,\text{red}} = \omega_i$

As we mentioned before, the reaction takes place via the saddle point located between U_{ox} and U_{red} . Let us define the equilibrium coordinates as:

$$\begin{aligned} q_1 &= Y_{1,\text{ox}} & q_1 &= Y_{1,\text{red}} \\ q_2 &= Y_{2,\text{ox}} & q_2 &= Y_{2,\text{red}} \end{aligned}$$

The Saddle point will correspond to

$$0 < \mu < 1$$

$$\begin{aligned} q_1^{\text{saddle}} &= Y_{1,\text{ox}} + \mu(Y_{1,\text{red}} - Y_{1,\text{ox}}) \\ q_2^{\text{saddle}} &= Y_{2,\text{ox}} + \mu(Y_{2,\text{red}} - Y_{2,\text{ox}}) \end{aligned}$$

8.15

The Saddle point is common to both potential energy surfaces, so:

$$e_{\text{ox}} + \sum \frac{1}{2} m_i \omega_i^2 \left[\mu (q_i - Y_{i,\text{ox}}) \right]^2 = e_{\text{red}} + \sum \frac{1}{2} m_i \omega_i^2 \left[(\mu - 1) (q_i - Y_{i,\text{red}}) \right]^2 \quad 8.16$$

where, $\mu = \frac{\lambda + e_{\text{red}} - e_{\text{ox}}}{2\lambda}$ 8.17 and $\lambda = \frac{1}{2} \sum m_i \omega_i^2 (Y_{i,\text{ox}} - Y_{i,\text{red}})^2$ 8.18
reorganisation energy

The activation energies can be expressed as:

$$E_{a,\text{ox}} = \frac{(\lambda + e_{\text{ox}} - e_{\text{red}})^2}{4\lambda} \quad 8.19 \quad E_{a,\text{red}} = \frac{(\lambda + e_{\text{red}} - e_{\text{ox}})^2}{4\lambda} \quad 8.20$$

and considering that the relative difference in the energies of reduced and oxidised species is determined by the overpotential

$$e_{\text{ox}} - e_{\text{red}} = -e\eta \quad 8.21$$

We finally get:

$$k_{\text{ox}} = A \exp \left[-\frac{(\lambda - e\eta)^2}{4\lambda kT} \right] \quad 8.22 \quad k_{\text{red}} = A \exp \left[-\frac{(\lambda + e\eta)^2}{4\lambda kT} \right] \quad 8.23$$

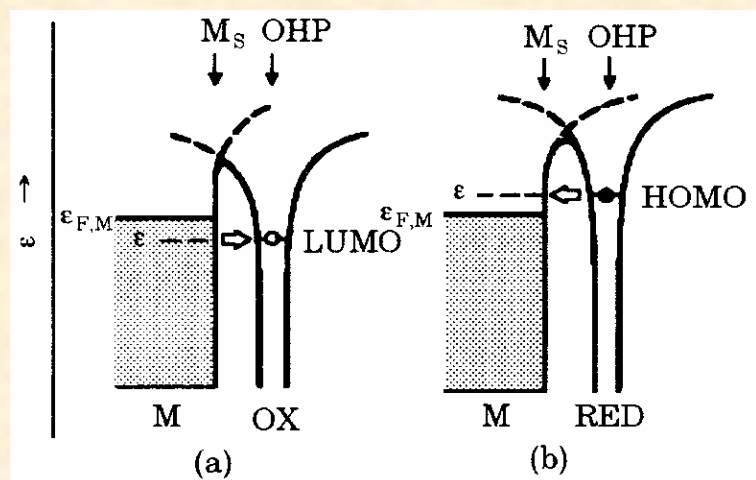
At the limit of low overpotentials $\lambda \gg |e\eta|$ eq. 8.22 can be simplified to:

$$k_{\text{ox}} = A \exp \left[-\frac{\lambda - 2e\eta}{4kT} \right] \quad 8.24$$

which has the same form of the Butler-Volmer expression with an activation energy of $\lambda/4$ at equilibrium and a transfer coefficient of 0.5. This approach lies at the centre of Marcus model for electron transfer. From here, we go on to obtain expressions for the solvent reorganisation energy in terms of the size of the redox species, distance from the electrode surface, dielectric constants and so on (see eq. 4.6) . On the other hand, the pre-exponential factor is determined by the electronic coupling between the redox species and the metal electrode. Again, only for outer-sphere electron transfer reactions, we have a fair understanding of this parameter. We will see all that later. What we have not addressed so far is the correlation between electron transfer rate and the overlap of the fluctuating energy levels (chapter 4) with the Fermi level of the metal.

The Gerischer's formulation

As we mentioned earlier, outer-sphere electron transfer takes place by isoenergetic tunnelling across the 0.3 to 0.5 nm compact layer. The rate of the reaction will depend on the density states occupied by the electron at the initial state and vacant for electrons in the final state.



$$v_t = k_t w_t D_{l,occ} D_{F,vac} \quad 8.25$$

Transmission coefficient k_t
 Tunnelling probability w_t
 State density in the initial state $D_{l,occ}$
 State density in the final state $D_{F,vac}$

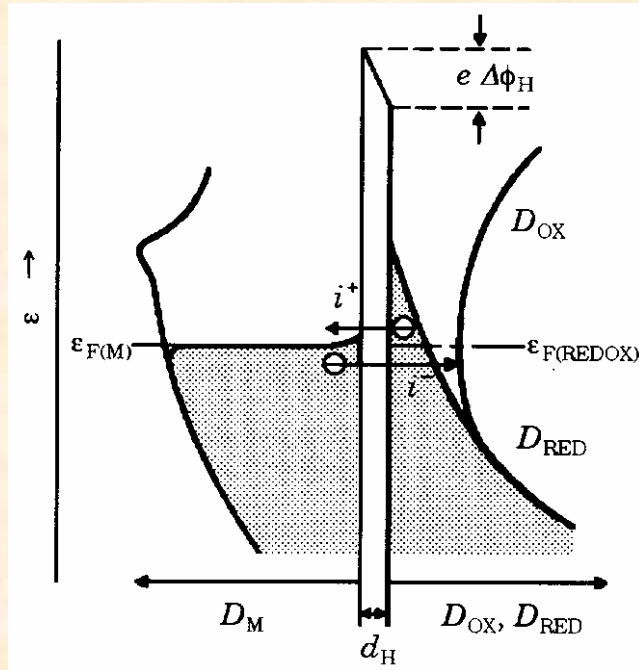
Eq. 8.26 reminds ourselves that the state density of electrons in the reduced and oxidised particles is given by the probability density distribution and the concentration of the particles (see eqs. 4.7-4.9):

$$D_{red}(E) = c_{red} W_{red}(E) \quad 8.26$$

$$D_{ox}(E) = c_{ox} W_{ox}(E)$$

while the total density is defined as: $D_{\text{redox}}(E) = D_{\text{red}}(E) + D_{\text{ox}}(E)$ 8.27

Similarly for the state density of electrons at the electrode: $D_M(E) = D_{M(e)}(E) + D_{M(h)}(E)$ 8.28



We can express the anodic and cathodic currents as a function of the energy level as:

$$i^+(E) = ek_t^+(E) D_{M(h)}(E) D_{\text{red}}(E) \quad 8.29$$

$$i^-(E) = ek_t^-(E) D_{M(e)}(E) D_{\text{ox}}(E) \quad 8.30$$

Electron tunnelling rate constant

Introducing the Fermi distributions, we obtain:

$$i^-(E) = ek_t^-(E) D_M(E) f(E - E_{F(M)}) D_{\text{redox}}(E) \left\{ 1 - f(E - E_{F(\text{redox})}) \right\} \quad 8.31a$$

$$i^+(E) = ek_t^+(E) D_M(E) \left\{ 1 - f(E - E_{F(M)}) \right\} D_{\text{redox}}(E) f(E - E_{F(\text{redox})}) \quad 8.31b \quad 13$$

The overall electron transfer current is obtained by integration of the microscopic current elements over the entire energy range:

$$i^- = \int_{-\infty}^{\infty} i^-(E) dE \quad i^+ = \int_{-\infty}^{\infty} i^+(E) dE \quad 8.32$$

In principle, we have now all the elements required to calculate the current associated with electron transfer.

Coming back to eq. 8.26, we can develop the probability density for the redox species as (see chapter 4):

$$W_{\text{red}}(E) = W_{\text{red}}(E_{\text{red}}) \sqrt{\frac{c_{\text{ox}}}{c_{\text{red}}}} \exp\left(-\frac{\lambda_{\text{red}}}{4kT}\right) \exp\left(-\frac{(1-\beta)(E - E_{F(\text{redox})})}{kT}\right) \quad 8.33$$

$$W_{\text{ox}}(E) = W_{\text{ox}}(E_{\text{ox}}) \sqrt{\frac{c_{\text{red}}}{c_{\text{ox}}}} \exp\left(-\frac{\lambda_{\text{ox}}}{4kT}\right) \exp\left(\frac{\beta(E - E_{F(\text{redox})})}{kT}\right) \quad 8.34$$

Symmetry factor $\lambda_{\text{ox}} = \lambda_{\text{red}}$
 $\beta = 0.5$

At the energy associated with the Fermi level of the redox species, $E_{F(\text{redox})}$

$$\frac{1}{2} D_{\text{redox}} E_{F(\text{redox})} = D_{\text{red}} E_{F(\text{redox})} = D_{\text{ox}} E_{F(\text{redox})} \quad 8.35$$

Consequently, we obtain from 8.33 to 8.35

$$D_{\text{red}}(E) = D_{\text{redox}}(E) f(E - E_{F(\text{redox})}) = D_{\text{red}}(E_{F(\text{redox})}) \exp\left(-\frac{(1 - \beta)(E - E_{F(\text{redox})})}{kT}\right)$$

$$= \frac{1}{2} D_{\text{redox}}(E_{F(\text{redox})}) \exp\left(-\frac{(1 - \beta)(E - E_{F(\text{redox})})}{kT}\right) \quad 8.36$$

$$D_{\text{ox}}(E) = D_{\text{redox}}(E) (1 - f(E - E_{F(\text{redox})})) = D_{\text{ox}}(E_{F(\text{redox})}) \exp\left(\frac{\beta(E - E_{F(\text{redox})})}{kT}\right)$$

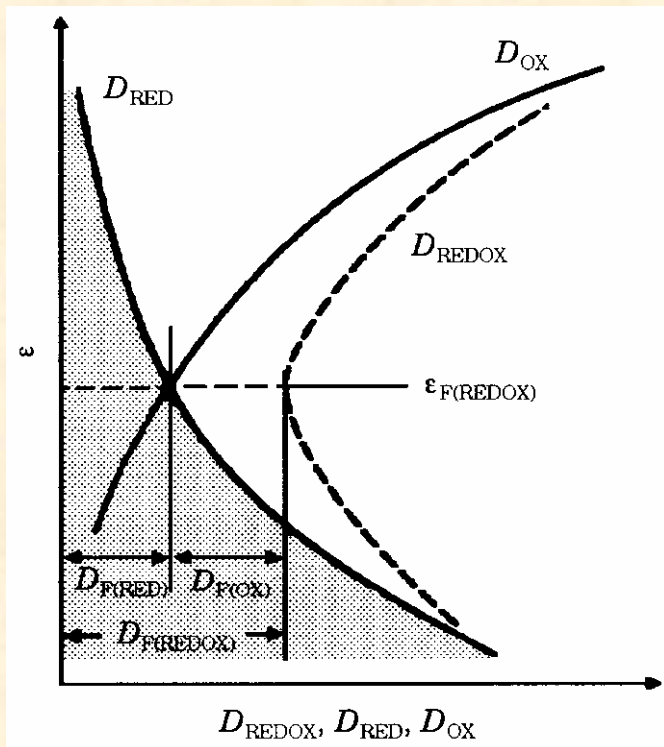
$$= \frac{1}{2} D_{\text{redox}}(E_{F(\text{redox})}) \exp\left(\frac{\beta(E - E_{F(\text{redox})})}{kT}\right) \quad 8.37$$

And the total state density: $D_{\text{redox}}(E) = D_{\text{red}}(E) + D_{\text{ox}}(E)$

$$D_{\text{redox}}(E) = \frac{1}{2} D_{\text{redox}}(E_{F(\text{redox})}) \left[\exp\left(\frac{\beta(E - E_{F(\text{redox})})}{kT}\right) + \exp\left(-\frac{(1-\beta)(E - E_{F(\text{redox})})}{kT}\right) \right]$$

8.38

Exchange Current Density



At equilibrium:

$$E_{F,M} = E_{F,\text{redox}}$$

$$i_o = i_o^- = i_o^+$$

$$k_t = k_t^+ = k_t^-$$

$$i_o(E) = i_o^+(E) = i_o^-(E)$$

Principle of microreversibility

From eqs 8.31a and 8.31b, we obtain

$$\begin{aligned}
 i_{\circ}^{-}(E) &= ek_t(E) D_M(E) f(E - E_{F(M)}) D_{\text{redox}}(E) \left\{ 1 - f(E - E_{F(\text{redox})}) \right\} = \\
 &= ek_t(E) D_M(E) \left\{ 1 - f(E - E_{F(M)}) \right\} D_{\text{redox}}(E) f(E - E_{F(\text{redox})}) = i_{\circ}^{+}(E)
 \end{aligned}$$

8.39

As usual, the exchange current is calculated by integrating over the energy range:

$$i_{\circ}(E) = \int_{-\infty}^{\infty} ek_t(E) D_M(E) f(E - E_{F(M)}) D_{\text{redox}}(E) \left\{ 1 - f(E - E_{F(\text{redox})}) \right\} dE \quad 8.40$$

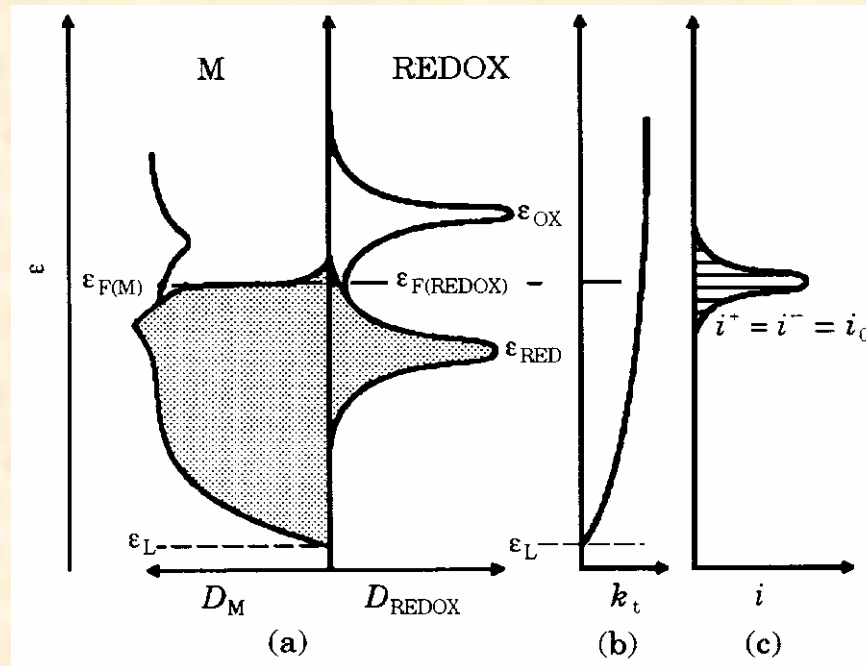
Further development of eq. 8.40 leads to:

$$i_{\circ} = ek_t(E_{F(M)}) D_M(E_{F(M)}) \frac{1}{2} D_{\text{redox}}(E_{F(\text{redox})}) B(\beta) \quad 8.41$$

where

$$B(\beta) = \int_{-\infty}^{\infty} \exp\left(\frac{\beta(E - E_{F(\text{redox})})}{kT}\right) f(E - E_{F(M)}) dE \approx \frac{\pi kT}{\sin\{(1 - \beta)\pi\}} \quad 8.42$$

17



90% of the integrand is 0.25 eV around the Fermi level. Finally, the exchange current density corresponds to:

$$i_0 \approx \frac{e\pi kT}{2 \sin\{(1-\beta)\pi\}} k_t \left(E_{F(M)} \right) D_M \left(E_{F(M)} \right) D_{redox} \left(E_{F(redox)} \right) \quad 8.43$$

Reaction Current Under Polarisation

Out of equilibrium, the Fermi levels are offset by the overvoltage: $E_{F(M)} = E_{F(\text{redox})} - e\eta$ 8.44

Under these conditions, $i(\eta) = i^+(\eta) - i^-(\eta)$ 8.45

$$i^-(\eta) = e \int_{-\infty}^{\infty} k_t(E, \eta) D_M(E) f(E - E_{F(\text{redox})} + e\eta) D_{\text{redox}}(E) \{1 - f(E - E_{F(\text{redox})})\} dE \quad 8.46$$

$$i^+(\eta) = e \int_{-\infty}^{\infty} k_t(E, \eta) D_M(E) \{1 - f(E - E_{F(\text{redox})} + e\eta)\} D_{\text{redox}}(E) f(E - E_{F(\text{redox})}) dE \quad 8.47$$

Introducing 8.36 and 8.37 into 8.46 and 8.47,

$$i^-(\eta) = ek_t(E_{F(M)}) D_M(E_{F(M)}) \frac{1}{2} D_{\text{redox}}(E_{F(\text{redox})}) \int_{-\infty}^{\infty} \frac{\exp\left(\frac{\beta(E - E_{F(\text{redox})})}{kT}\right)}{1 - \exp\left(\frac{E - E_{F(\text{redox})} + e\eta}{kT}\right)} dE \quad 8.48$$

$$i^-(\eta) = i_0 \frac{k_t(E_{F(M)})}{k_t(E_{F(\text{redox})})} \exp\left(\frac{-\beta e\eta}{kT}\right) \quad 8.49$$

$$i^+(\eta) = ek_t(E_{F(M)}) D_M(E_{F(M)}) \frac{1}{2} D_{\text{redox}}(E_{F(\text{redox})}) \int_{-\infty}^{\infty} \frac{\exp\left(\frac{-(1-\beta)(E - E_{F(\text{redox})})}{kT}\right)}{1 - \exp\left(\frac{E_{F(\text{redox})} - E - e\eta}{kT}\right)} dE$$

$$i^+(\eta) = i_0 \frac{k_t(E_{F(M)})}{k_t(E_{F(\text{redox})})} \exp\left(\frac{(1-\beta)e\eta}{kT}\right) \quad 8.51$$

8.50

