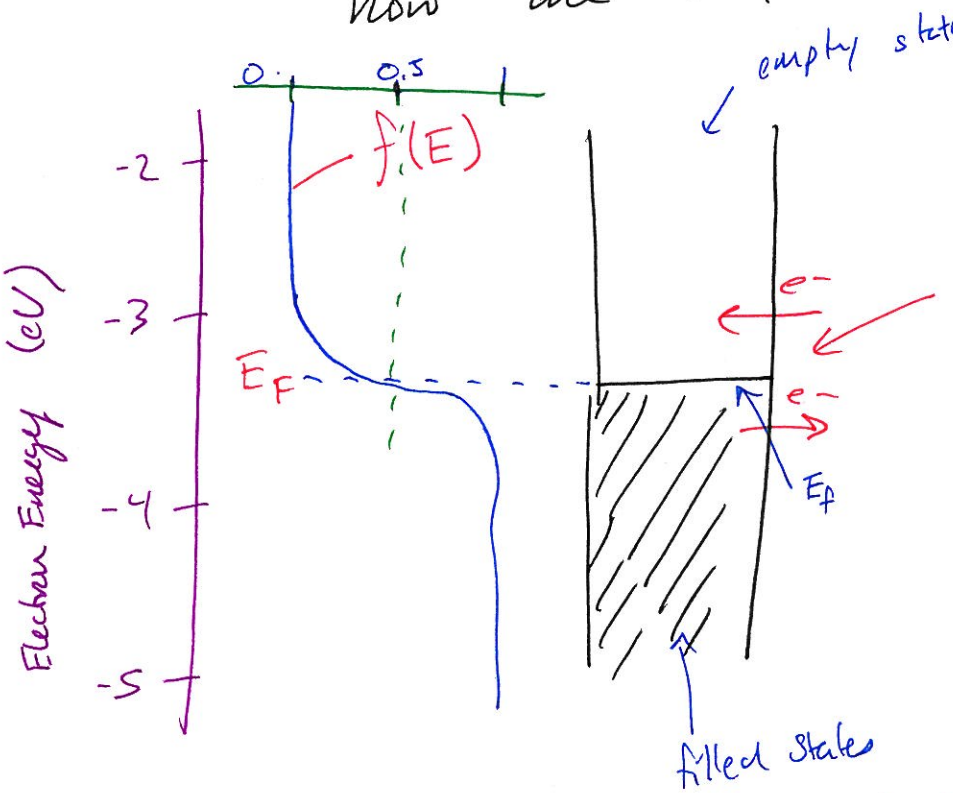
3.6.3 Marcus - Gerischer Model

What do the electronic states look like in a metal and how are they filled?



Q. how abrupt is the transition from filled to empty states?

A: depends on Temperature...

$\pm 3kT$

Which states contribute to electron transfer reactions?
empty states → can accept electrons, filled states can donate electrons.

$f(E)$ is the Fermi function that describes the state filling

$$f(E) = \frac{1}{1+e^{(E-E_f)/kT}}$$

where E is an energy state inside the material → not the Electrode potential!

So we can now understand the states in the electrode

# of states in energy range between E and E+dE is:

$$\text{states} = A\,\rho(E)\,dE = \text{total number of states}$$

area exposed to solution (cm^2)

density of states (ie states per unit area per energy interval) ($cm^{-2}eV^{-1}$)

eV interval

But not all those states are occupied...

$$\text{number of occupied states} = A\,N_{occ}(E)\,dE$$

where $N_{occ}(E) = f(E)\,\rho(E)$

$f(E)$ is the fermi function and says whether or not a state is occupied.

Similarly $N_{unocc}(E) = [1 - f(E)]\,\rho(E)$

is the density of unoccupied states

Q. So what happens when change the potential of the electrode?

A. On Metal, the states all shift up or down by the effect of the electrostatic potential.

→ so the same set of states exist near the Fermi level at all potentials.

Those states move up and down in energy relative to the states in the solution as a function of electrode potential.

Now we need to consider the electronic states in the solution using similar formalism to understand transfer back and forth.

in the solution filled and empty

states correspond to different chemical species (O and R)

Different than metal states as they are localized ...

$D_R(\lambda, E)$ is called the concentration density function (units of $cm^{-3} eV^{-1}$)

Note: this is just the density of states in the solution!

So that the <u>number concentration</u> of R is: $D_R(\lambda, E)\,dE$ over a given dE

We can factor $D_R(\lambda, E)$ into different components.

$$D_R(\lambda, E) = N_A\, C_R(0,t)\, W_R(\lambda, E)$$

avogadros number

concentration of R at the electrode surface.

Probability density function (analogy to fermi-function in solids)

$$\int W_R(\lambda, E)\, dE = 1$$

as $\int D_R(\lambda, E)\, dE = N_A C_R(0,t)$

So $W_R(\lambda, E)$ is a normalized function.

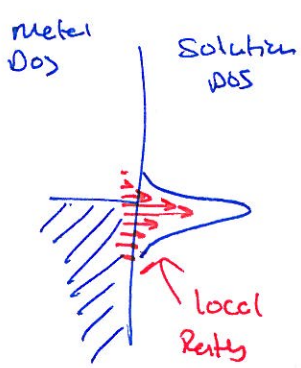
* Similarly $D_O(\lambda, E) = N_A C_O(0,t)\, W_O(\lambda, E)$

* Now consider the rate at which O is reduced by electrons in occupied states on the electrode

$$\text{Local Rate}(E) = \frac{\overbrace{\varepsilon_{red}(E)}^{\text{proportionality constant describing probability of the transition}} \overbrace{D_o(\lambda, E)}^{\text{density of states of O in solution}} A \overbrace{N_{occ}(E)}^{\text{density of occupied states in solid}} dE}{\Delta t}$$

where Δt is very short time on the scale of $\frac{1}{\nu}$ where ν is the vibrational frequency of the molecule.

to get the overall rate we need to integrate the local rate expression



$$\Delta t = \frac{1}{\nu}$$

$$\text{Rate} = \nu \int_{-\infty}^{\infty} \varepsilon_{red}(E) D_o(\lambda, E) A N_{occ}(E) dE$$

write this out explicitly

$$\text{Rate} = \nu A N_A C_o(0,t) \int_{-\infty}^{\infty} \varepsilon_{red}(E) w_o(\lambda, E) f(E) \rho(E) dE$$

units = $\frac{\text{electrons or molecules}}{s}$

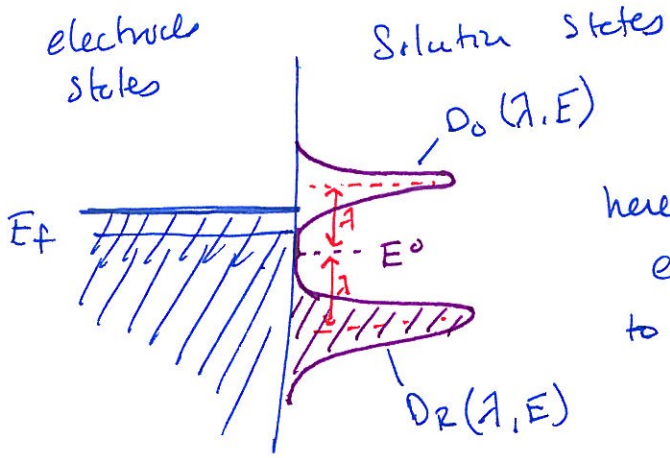
We can thus express the conventional rate constant for this reaction as:

$$k_f = \nu \int_{-\infty}^{\infty} \varepsilon_{red}(E)\, \underbrace{W_O(\lambda, E)}_{\text{solution acceptor states}}\, \underbrace{f(E)\, p(E)}_{\text{filled electrode states}}\, dE$$

transition probability

$$k_b = \nu \int_{-\infty}^{\infty} \varepsilon_{ox}(E)\, W_R(\lambda, E)\, [1 - f(E)]\, p(E)\, dE$$

<u>Key concept:</u> must have overlapping distributions of states in the electrode and in the solution in order to get <u>significant rates</u>.



here: what do we expect the net rate to be? Will we do reduction of $O \to R$ or oxidation of $R \to O$?

Marcus Theory and the solution probability Densities

We wrote earlier that

$$\Delta G_f^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{F(E - E^{\circ})}{\lambda}\right)^2$$

this is for an electron sitting at an energy $\underline{E}$ ⇒ now we have a distribution of energies.

So the maximum rate will be for electrons that are at an energy $\underline{E = E^{\circ} + \lambda}$

so $\underline{\Delta G_f^{\ddagger} = \phi}$

From Marcus Theory

$k_f = K_{p,o} \nu_n K_{el} \exp(-\Delta G_f^{\ddagger}/kT)$

therefore

$$\frac{\text{Local Rate @ } E_f = E}{\text{Max local rate @ } (E_f = E^{\circ} + \lambda)} = \frac{\exp\left[-\frac{\lambda}{4kT}\left(1 - \frac{E - E^{\circ}}{\lambda}\right)^2\right]}{\exp\left[-\frac{\lambda}{4kT}\left(1 - \frac{E^{\circ} + \lambda - E^{\circ}}{\lambda}\right)^2\right]}$$

$$= \exp\left[\frac{-\lambda}{4kT}\left(1 - \frac{E - E^{\circ}}{\lambda}\right)^2\right]$$

this must be equal to the rates just derived

these factors are similar and can cancel out

$$= \frac{\varepsilon_{red}(E)\, D_o(\lambda, E)\, f(E_f)\, \rho(E_f)}{\varepsilon_{red}(E^{\circ} + \lambda)\, D_o(\lambda, E^{\circ} + \lambda)\, f(E_f)\, \rho(E_f)}$$

these cancel out because states at E_f do not depend on the electrode potential

Therefore: $$\frac{D_0(\lambda, E)}{D_0(\lambda, E^0+\lambda)} = \underbrace{\exp\left[\frac{-(E-E^0-\lambda)^2}{4\lambda kT}\right]}$$

gaussian distribution centered $E = E^0 + \lambda$ with a standard deviation of $(2\lambda kT)^{1/2}$

now $$\frac{D_0(\lambda, E)}{D_0(\lambda, E^0+\lambda)} = \frac{N_A C_0(0,t)\, W_0(\lambda, E)}{N_A C_0(0,t)\, W_0(\lambda, E^0+\lambda)}$$

$$= \boxed{\frac{W_0(\lambda, E)}{W_0(\lambda, E^0+\lambda)}} = \exp\left[\frac{-(E-E^0-\lambda)^2}{4\lambda kT}\right]$$

Since normalized function, $W_0(\lambda, E^0+\lambda) = (2\pi)^{-1/2} \cdot \frac{1}{\text{Stand. Dev}}$

So $$\boxed{W_0(\lambda, E) = (4\pi\lambda kT)^{1/2} \exp\left[\frac{-(E-E^0-\lambda)^2}{4\lambda kT}\right]}$$

$$\boxed{W_R(\lambda, E) = (4\pi\lambda kT)^{1/2} \exp\left[\frac{-(E-E^0+\lambda)^2}{4\lambda kT}\right]}$$

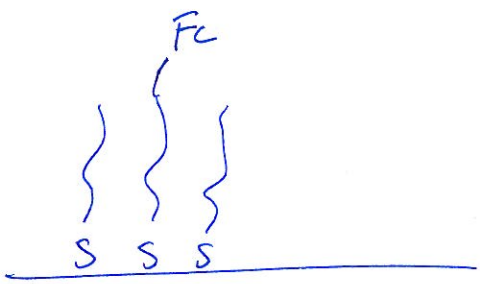
So this justifies the exponential distribution

3.6.4. Tunnelling

* Charge transfer indeed takes place some distance into the solution

probability of tunnelling $\boxed{\propto \exp(-\beta x)}$

* β depends on height of the tunnelling barrier as well as well as the medium through which tunnelling occurs.



$\beta \sim 1$ to $1.2\ \text{Å}^{-1}$ for through-bond tunnelling (less for conjugated systems) more for vacuum