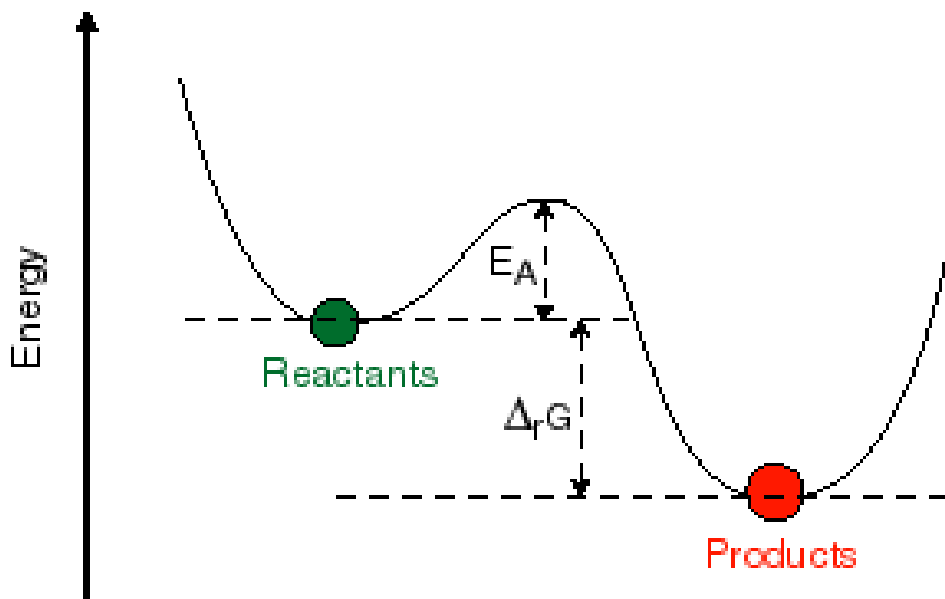# The Marcus Theory of Electron Transfer

A great many important aspects of biology and biochemistry involve electron transfer reactions. Most significantly, all of respiration (the way we get energy from food and oxygen) and photosynthesis (they way plants make the food and oxygen we consume) rely entirely on electron transfer reactions between cofactors in proteins. These are basically nanoscale electronic devices, in a rather molecular sense, whose job it is to push electrons and protons around and in so doing convert energy from one form to another.

The other reason to study electron transfer is that it is a very simple kind of chemical reaction and in understanding it, we can gain insight into other kinds of chemistry and biochemistry. After all, what is chemistry but the moving of electrons from one place to another?
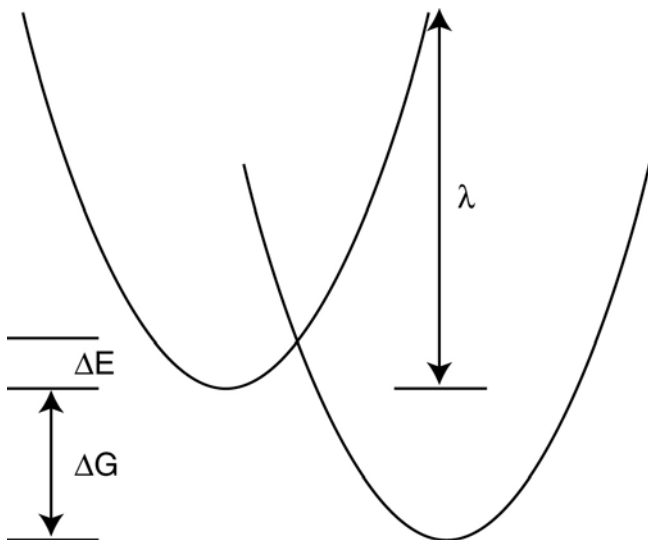

OK, so you guys have all seen pictures of potential surfaces (above). We had some of these in the lectures on kinetics when we talked about kinetic theory. We start with the reactant state and have to go over a hill to get to the product state. The y axis is energy. The more mysterious x axis is something called a reaction coordinate which includes somehow all the changes that occur in the positions of nuclei as we go from reactants to products. The hill in the middle is the activation energy. Recall that given this kind of system, the rate constant of the reaction is given by

$$k \propto e^{-E_A / k_B T}$$

OK, well at one point about 50 years ago a guy named Rudy Marcus decided that for something simple like electron transfer, maybe you could take this picture literally and draw two parabolas. These two parabolas represented the energy of the reactant as the nuclei moved around and the energy of the product as the nuclei moved around. The reason why it is a parabola is that this is the relationship you would get if the nuclei were

connected by springs to each other (remember Hooke's law from Physics?). In this case the energy is just dependent on the square of the distance you either stretch or compress the springs from their equilibrium positions. The reactant and product have different equilibrium nuclear positions (x axis values) because in electron transfer the charge on the atoms or molecules involved changes and therefore the attraction or repulsion of the things being held by the springs changes so the spring is either more compressed or more expanded.

In this picture ΔG is the free energy change between the reactants on the left and the products on the right and ΔE is the activation energy. λ is the reorganization energy. This is the energy it would take to force the reactants (on the left) to have the same nuclear configuration as the products (on the right) without letting the electron transfer.

All Marcus did was realize that he could solve for the point of crossing between the parabolas and derive the activation energy (and thus the rate constant) from the thermodynamic parameters of the system. So let's do this. You don't need to actually do this derivation on the test, but you need to understand what is being done and why.

Let's assume that the bottom of the left parabola is at (0,0) and its equation is $y = x^2$. This is completely general because we have not assigned any scale to the axes. If this is true, and if we assume that the shape of the second parabola is the same as the first and it is just displaced, then the equation of the second parabola is just $(y-b) = (x-a)^2$. In other words, the bottom of the second parabola is at the point (a,b). All we have to do is solve for the y value that the two are equal and we will know the activation energy.

$$y = x^2$$

$$(y - b) = (x - a)^2$$

$$y = x^2 - 2ax + a^2 + b$$

combining

$$x^2 = x^2 - 2ax - a^2 + b$$

$$0 = -2ax - a^2 + b$$

$$2ax = b - a^2$$

$$x = \frac{(b - a^2)}{2a}$$

or from the first equation :

$$y = x^2 = \frac{(b - a^2)^2}{4a^2}$$

Now remember that the y value of the intersection of the two parabolas is just ΔE (so what we just calculated is ΔE). In addition, b is the displacement between the two parabolas in the y direction and that is just ΔG. Finally, a is the displacement between the two parabolas in the x direction and thus a^2 is λ. Plugging all of this in we have:

$$\Delta E = \frac{(\Delta G + \lambda)^2}{4\lambda}$$

And the rate constant is just given by

$$k = Ae^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT}}$$

The preexponential factor, A, is often expressed as an exponential term itself, dependent on the distance, r, between the molecule or group that donates the electron and the one that accepts it:

$$k = ce^{-\beta r}e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT}}$$

Where 'c' is just another constant. β is a constant which depends on what is between the donor and acceptor of the electron. Basically, electrons go through some materials much more easily than others and β just reflects this.

I expect you to be able to analyze the rate of an electron transfer reaction given the properties of that reaction (the free energy, the reorganization energy, β, temperature, etc.), just as you did before activation energies, rates and temperatures in a previous

chapter. You should also be able to tell what is what on the diagrams like the ones shown in at the top of this file. You are not responsible for the derivation of the Marcus equation.

Some sample questions

1) What is the physical meaning of the reorganization energy?

2) What is the relationship between the free energy change and the reorganization energy when the rate constant is maximal?

3) Does rate always increase as the free energy change becomes more negative?

4) If I increase the distance between the electron donor and acceptor by 5 angstroms, I find that the rate constant for a particular electron transfer reaction decreases by 10-fold. What is β?

5) I find that at 37 C the rate constant for a particular electron transfer reaction is twice what it is at 0 C. Assuming that the equilibrium constant for the reaction is about 100 (favoring the product) and roughly independent of temperature over this range, what is the reorganization energy for this reaction (assume $\Delta G = \Delta G^0$ for this reaction)?

Answers are on the next page

1) It is the amount of energy required to distort the nuclear configuration of the reactants into the nuclear configuration of the products without electron transfer occurring.

2) The maximum rate constant for electron transfer occurs when the free energy is equal and opposite to the reorganization energy. Remember, the free energy for a spontaneous electron transfer is negative and the reorganization energy is positive. At some point the sum will be zero. Because the sum is squared, the exponent is negative, the function will be maximum at this point.

3) No, it decreases once you have past the point where it just cancels out the reorganization energy.

4) As can be seen above,

$$k = ce^{-\beta r}e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT}}$$

we also know that

$$0.1k = ce^{-\beta(r+5)}e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT}}$$

taking the ratio

$$0.1 = \frac{e^{-\beta(r+5)}}{e^{-\beta r}} = e^{-5\beta}$$

$$\beta = 0.46$$

This is an important number in the field of electron transfer in proteins and other biological materials. It is one of the ways of characterizing the electron transfer reaction.

5) The standard free energy for the reaction is $-RT\ln K_{eq} = -11.3$ kJ/mole $= \Delta G^0$
So we have

$$k = ce^{-\beta R}e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT_1}}$$

and at T2

$$2k = ce^{-\beta R}e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT_2}}$$

taking the ratio

$$2 = \frac{e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT_2}}}{e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT_1}}} = e^{\frac{-(\Delta G + \lambda)^2}{4\lambda RT_2} + \frac{(\Delta G + \lambda)^2}{4\lambda RT_1}}$$

When I solve this for the reorganization energy, I get about 91 kJ/mole