# A note on rates and units of measurement relevant to charge transfer

Consider the reaction of A → B
(this can be any reaction, but for this document it primarily represents the reaction of charge transfer. Specifically A represents the state with the electron on the donor, and B represents the state with the electron on the acceptor.)

One can track the population (or concentration) of A and B over time. Denoted by [A](t) and [B](t). Since charge transfer is a single step reaction, then a single rate constant can be assigned, k, such that:

$$\frac{d[A]}{dt} = -k[A]$$

and:

$$\frac{d[B]}{dt} = +k[A]$$

If we start with [A](0) = 1 and [B](0) = 0, then the solutions are (check for your self):

$$[A](t) = [A](0)\exp(-kt)$$

and

$$[B](t) = 1 - [A](0)\exp(-kt)$$

So A exponentially decays, converting to B with a rate constant of k. But what are the units of k, ,and what does it tell us? Whether [A] and [B] are in units of molar, population, etc, dimensional analysis tells us that k should have units of inverse time. For example, one might write k = 12 ns$^{-1}$, which would be equivalent to k = 1.2 x 10$^{10}$ s$^{-1}$ (check this!).

When discussing charge transfer rates and rate constants, it is not uncommon to refer to something called the "time constant" or $\tau$ (tau). This is simply the inverse of the rate constant, k. So k = 12 ns$^{-1}$ corresponds to $\tau$ = 83 ps (check this!).

A convenient way to think of tau, is that it corresponds to the time when the exponentially decaying populations has been diminished to ~1/3 of its original value. Specifically, [A]($\tau$) = 1/e.

# Molecular charge transfer theory: key parameters are distance and driving force

**Distance**
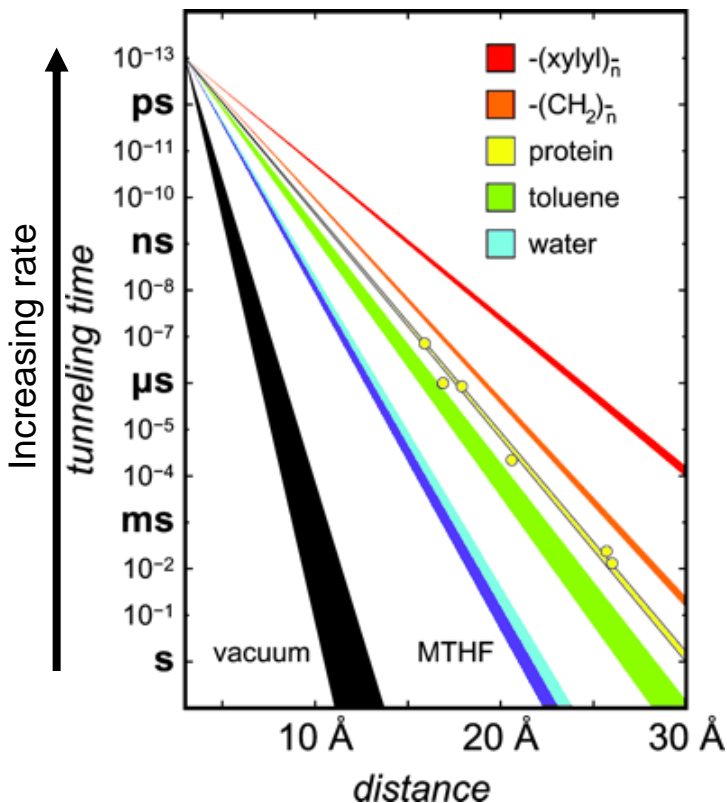


**Driving Force**

charge transfer
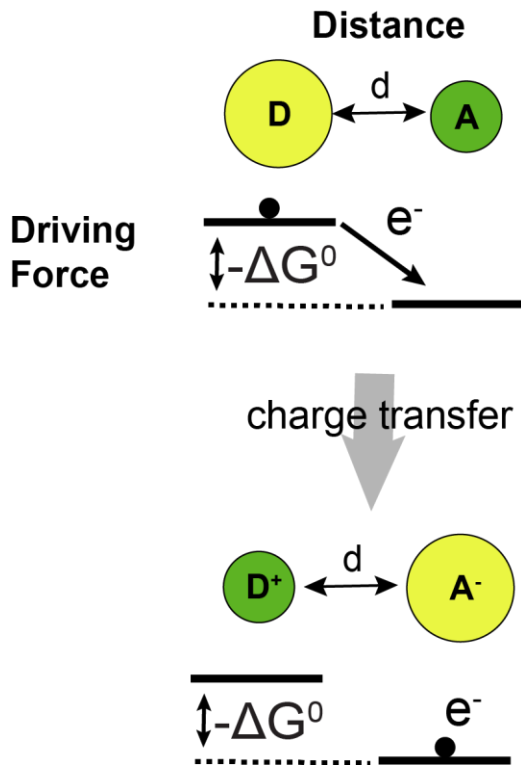
**Key parameters:**

**Distance (d) –**
Physical distance between donor (D) and acceptor (A)
(e.g. 1 nm)

**Driving Force (-ΔG⁰) –**
Free energy difference between initial state (charge on donor) and final state (charge on acceptor)

## Increasing the physical distance decreases the charge transfer rate



Distance dependence comes from electron tunneling

$$k_{ct} = k_0 \exp\left(-\beta d\right)$$

(Value of $\beta$ depends on medium)

The exponential decrease in rate with distance comes directly from the exponential fall off of a particle's wave function into a barrier (from introductory quantum mechanics).

Gray, H.B; Winkler, J.R. *Proc. Natl. Acad. Sci.* **2005**, *102*, 3534-3539

# Increasing the driving force does not necessarily increase the charge transfer rate

## "Marcus Theory"

Log(rate)

$\lambda$

$-\Delta G^0$
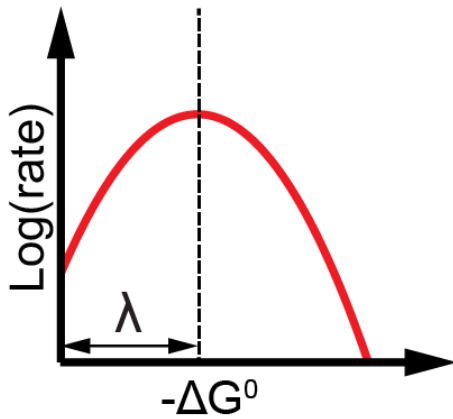
It turns out that the rate increases for small driving forces, then decreases at large driving forces. This is a bit surprising and it is worth explaining why this happens. First shown by Rudy Marcus in the 1950s, this work was awarded the Nobel Prize for Chemistry in 1992.
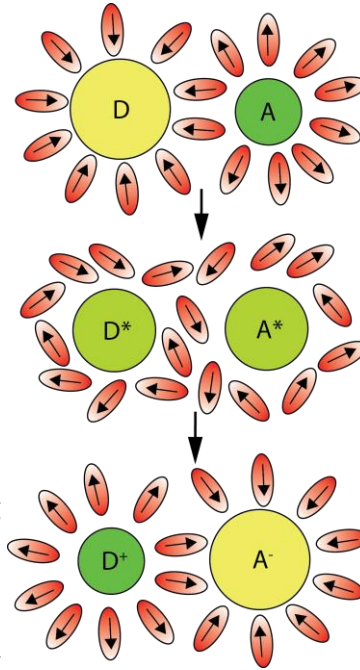
## Nuclear reorganization dictates driving force dependence

The key to understanding how the driving force impacts charge transfer rate is to realize that upon charge transfer from D (donor) to A (acceptor), nuclei will need to rearrange to accommodate the movement of charges. The bonds may expand in the acceptor and contract in the donor. Furthermore, polar solvents will reorient their dipoles. This nuclear reorganization dictates the activation energy, which in turn determines the rate of charge transfer.

The following diagram includes curves showing the free energy of the entire system (D and A and solvent molecules) in two situations: When the electron is on the donor (red) and when the electron is on the acceptor (blue). You could also think of this as the initial state (red) and final state (blue). The x-axis denotes different nuclear configurations, and encompasses the positions of many many atoms as they move from the stable configuration for the electron on the donor (red curve minimum) to the stable configuration with the electron on the acceptor (blue curve minimum). In the diagram below, there is no net driving force for charge transfer. However, there is still an activation energy, which dictates the rate (via an Arrhenius relationship):

$$rate = A * e^{-E_{act}/kT}$$

DA

$D^+A^-$

energy

$E_{act}$

nuclear arrangement
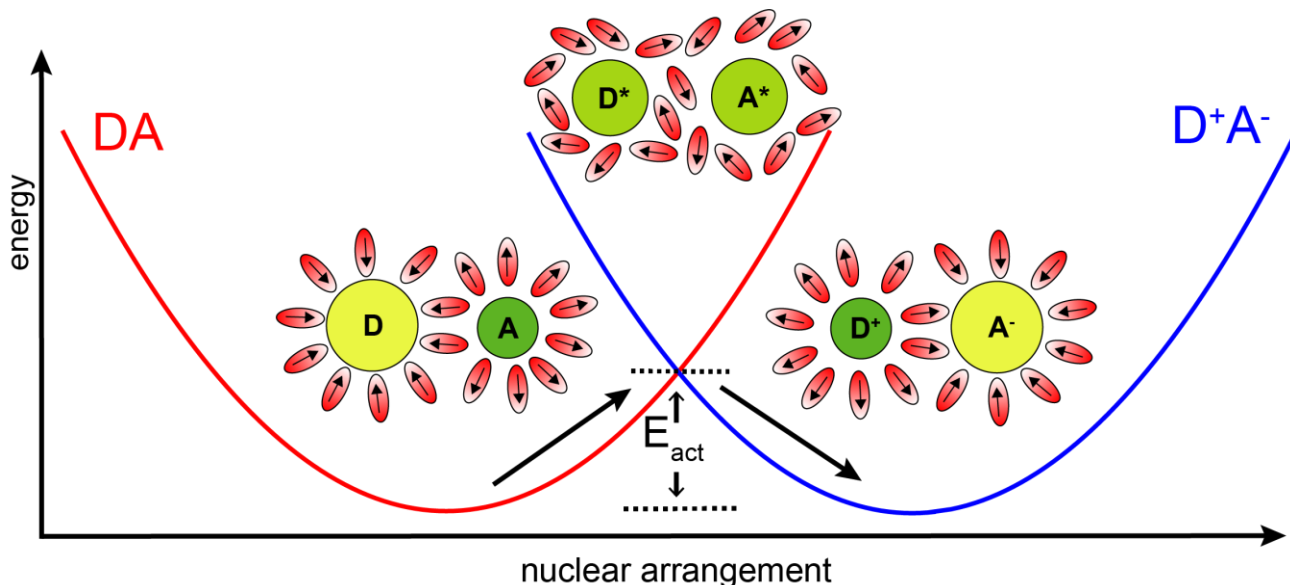
Why does the electron transfer when the curves cross? Electrons move much faster than nuclei (Born-Oppenheimer approximation), so when electron transfer happens vibrations and nuclear movement will not be fast enough to accommodate any energy lost or gained by the electron. In the absence of other free electrons, the electron transfer must happen between two states with equal energy and equal nuclear arrangement. Therefore, electron transfer occurs when the curves cross.

# Driving force changes manifest in activation energy changes

## And rate is dependent on activation energy (see Arrhenius relation)
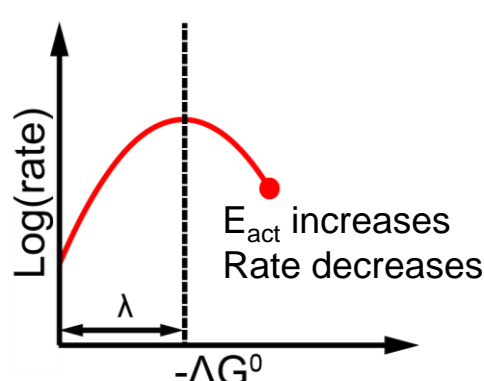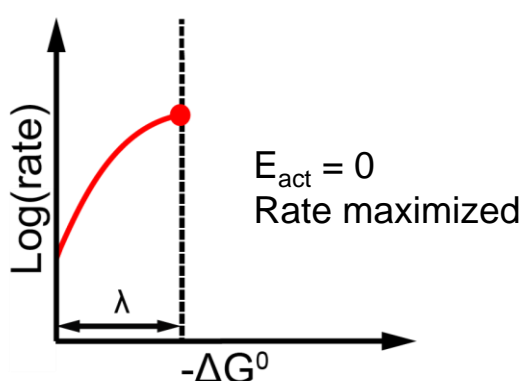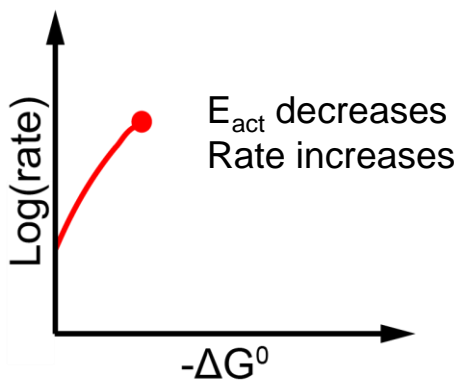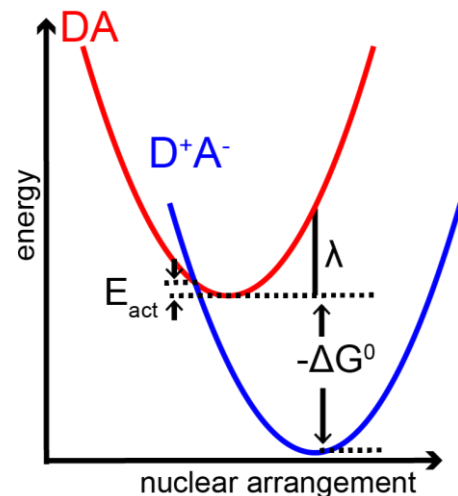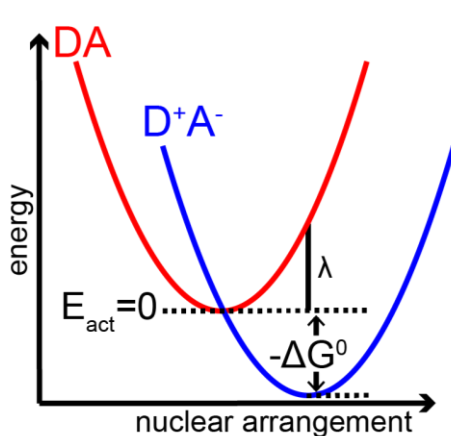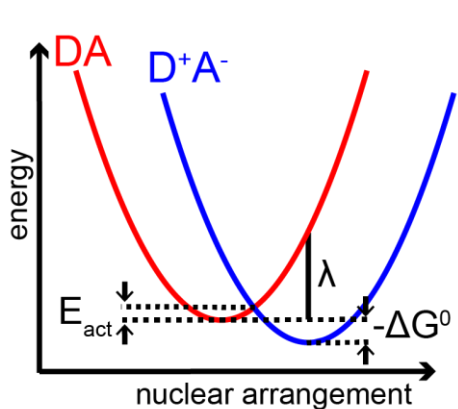


Bonus points: Use parabolic equations to show that $E_{act} = \dfrac{(\lambda + \Delta G^0)^2}{4\lambda}$
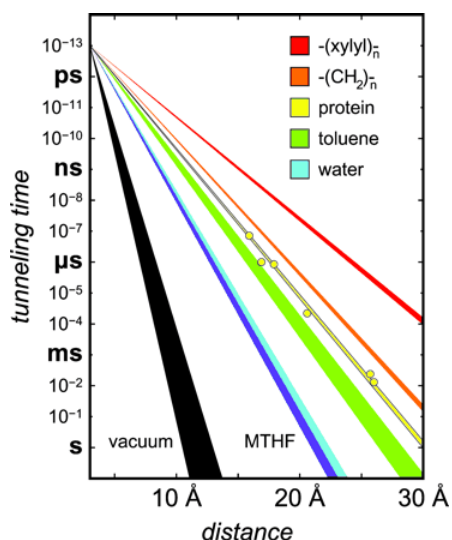
# Overview of key parameters in the Marcus equation

$$k_{ct} = \frac{2\pi}{\hbar}|V_0|^2 exp(-\beta\boldsymbol{d}) * \frac{1}{\sqrt{4\pi\lambda k_B \boldsymbol{T}}} exp\left(-\frac{(\lambda + \boldsymbol{\Delta G^0})^2}{4\lambda k_B \boldsymbol{T}}\right)$$
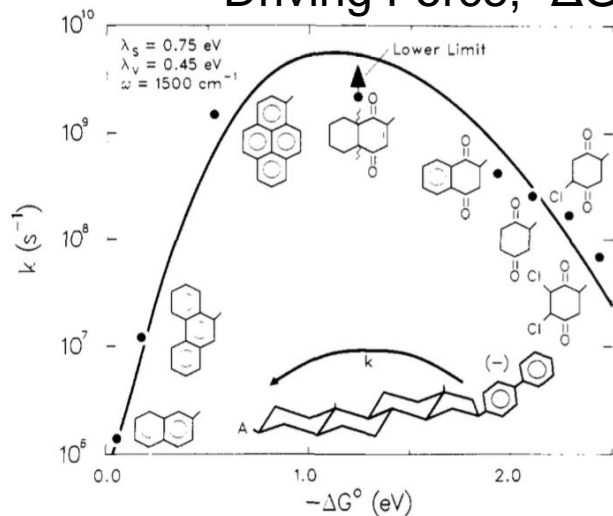
**Electron tunneling**

**Nuclear Reorganization**

Distance, d

Driving Force, $-\Delta G^0$

# How does this all translate to photoexcited charge transfer?

In photoexcited charge transfer, the initial state is generated by photoexcitation. Typically, an electron is promoted to a higher energy level in a molecular (i.e. from the HOMO to the LUMO). This electron then falls to a lower energy state on another nearby molecules, in a charge transfer process (described in previous slides).
One slightly confusing aspect of photoexcited charge transfer is the use of both "electron transfer" and "hole transfer". The only real difference between these is whether the electron donor or acceptor is initially photoexcited. See the diagram below:

1. Photoexcitation; 2. charge separation; 3. charge recombination



Electron transfer

Hole transfer