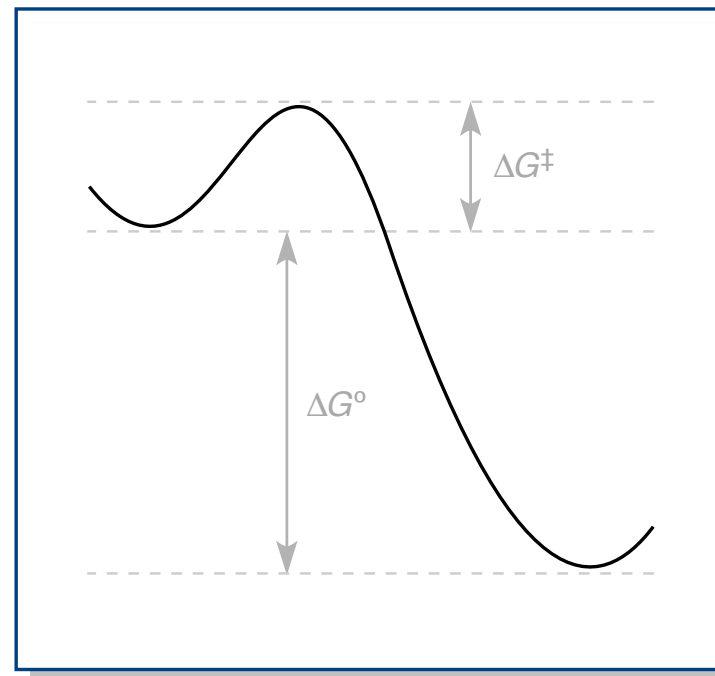
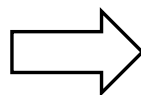
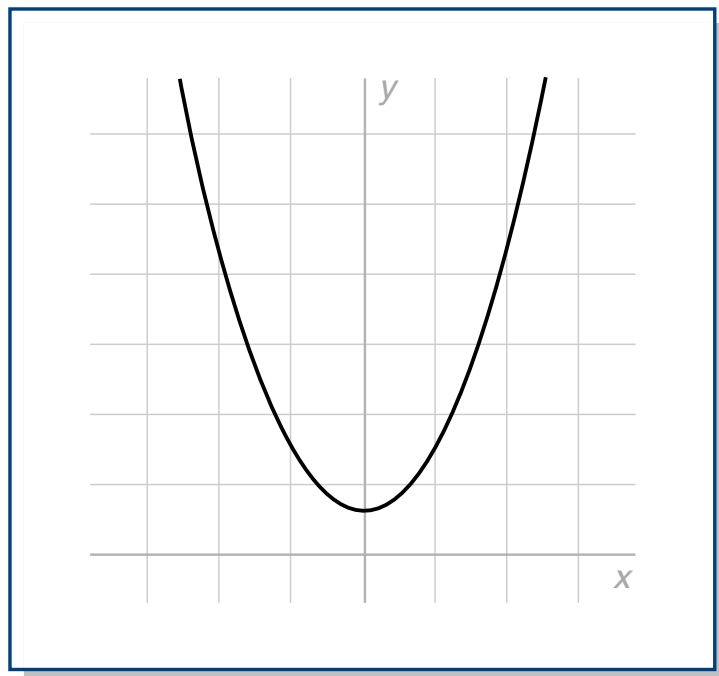


A Very Brief Introduction to the Concepts of Marcus Theory



Valerie Shurtleff
MacMillan Group Meeting
January 26, 2016

Rudolph "Rudy" A. Marcus

- Born July 21, 1923 in Montreal, Canada
- B.Sc. in chemistry from McGill University, 1943
- Ph.D. in chemistry from McGill University, 1946
- Postdoctoral work at National Research Council of Canada and University of North Carolina
- Assistant Professor to Professor, Polytechnic Institute of Brooklyn, 1951–1964
- Professor, University of Illinois at Urbana–Champaign, 1964–1978
- Arthur A. Noyes Professor of Chemistry, Caltech, 1978–2012
- Nobel Prize in Chemistry, 1992
- John G. Kirkwood and Arthur A. Noyes Professor of Chemistry, Caltech, 2013–present



Marcus Theory: Where Did It Come from, and What is It Good For?

Marcus theory

Originally introduced by R. A. Marcus in 1956 as a method for calculating rates of electron transfer in outer-sphere processes. It has since been extended and refined significantly to address a variety of different types of transformations.

Where has this theory found the most utility?

- electron transfer between inorganic, organometallic, and organic molecules
- electron transfer in proteins
- atom-transfer processes: hydrogen atom transfer, PCET
- proton-transfer reactions
- group-transfer reactions, e.g. S_N2 reactions

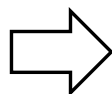
Breaking Down a Reaction Coordinate Diagram

What are the "wells" on a potential energy curve?

reactants

products

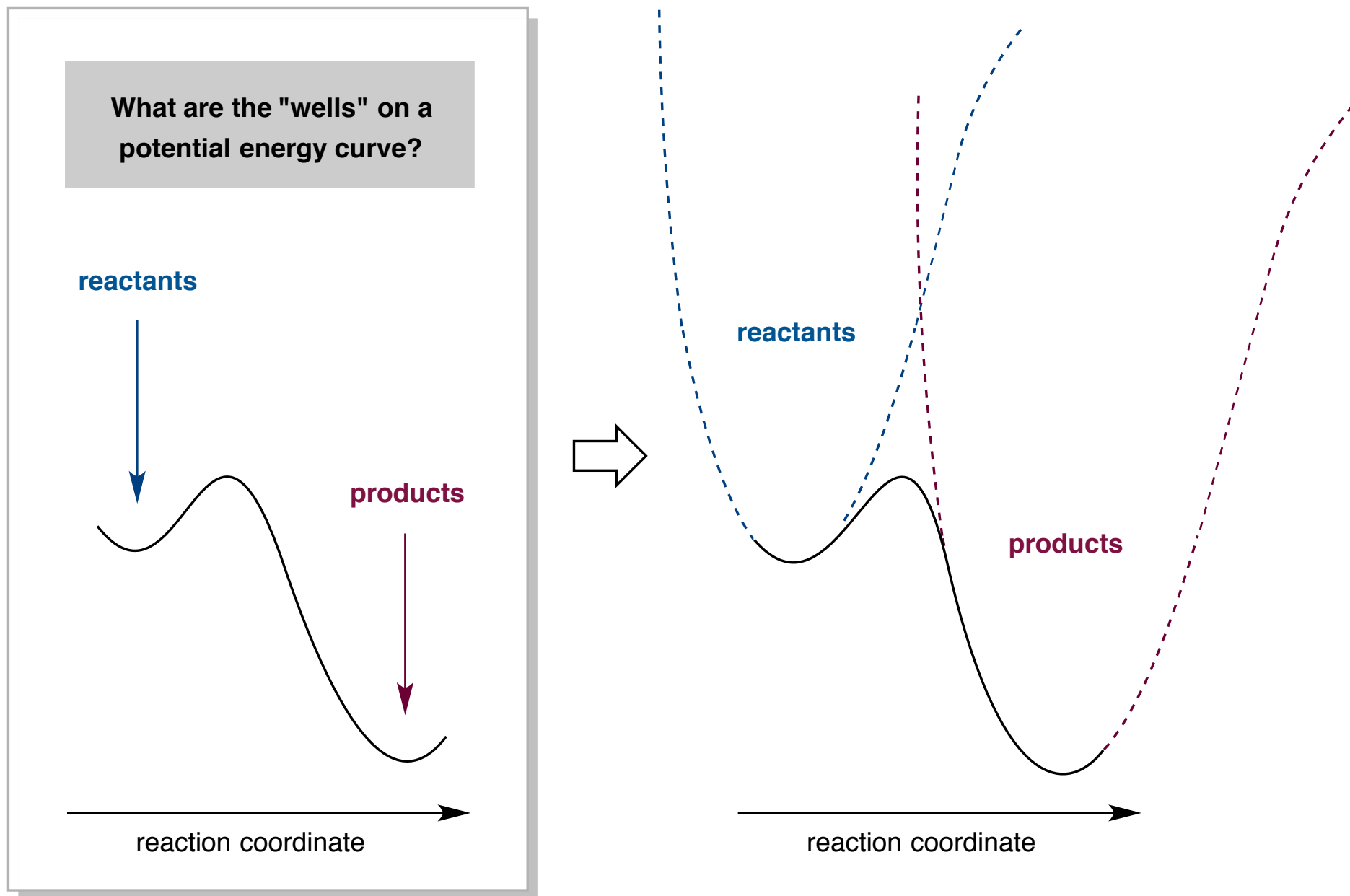
reaction coordinate



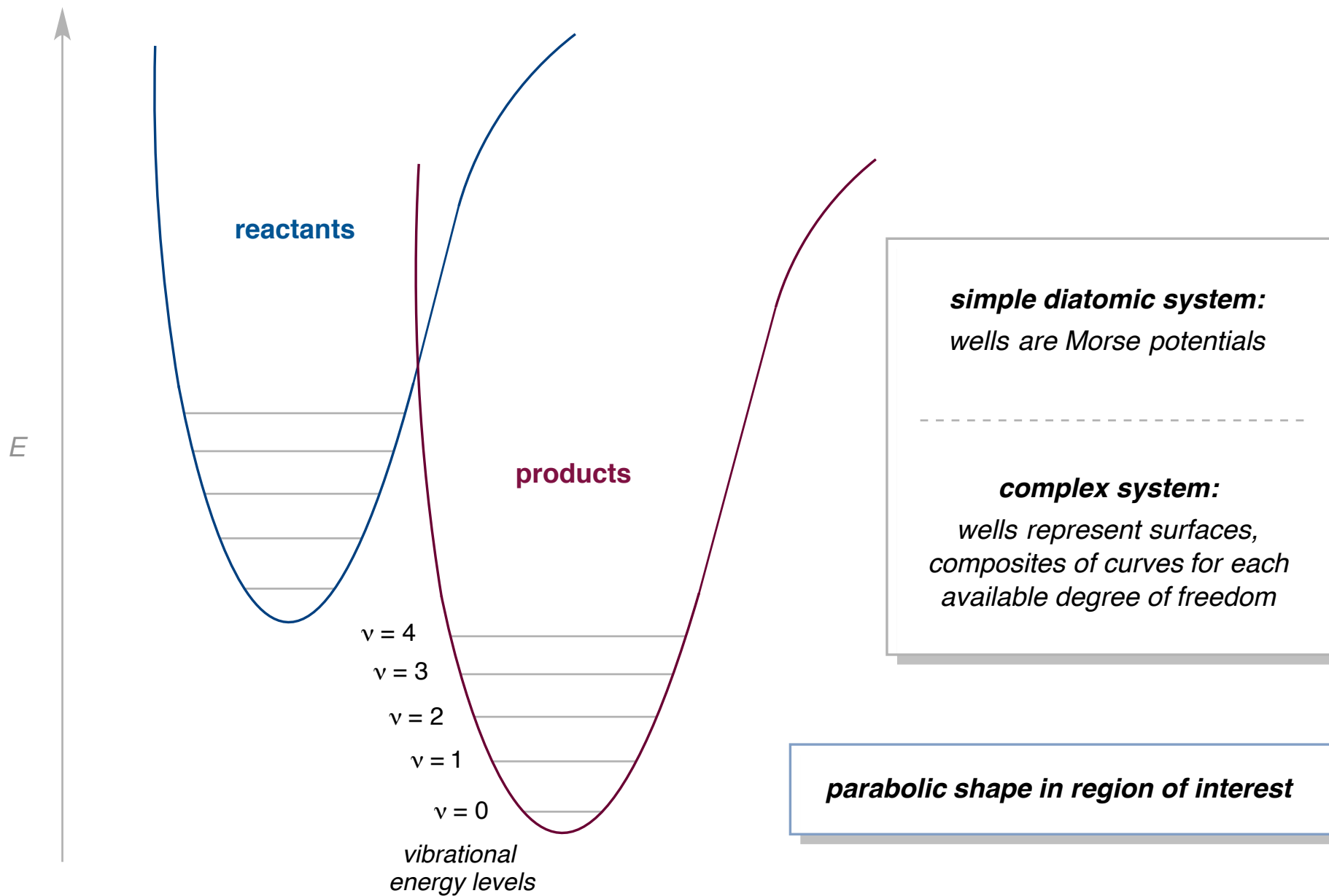
reactants

products

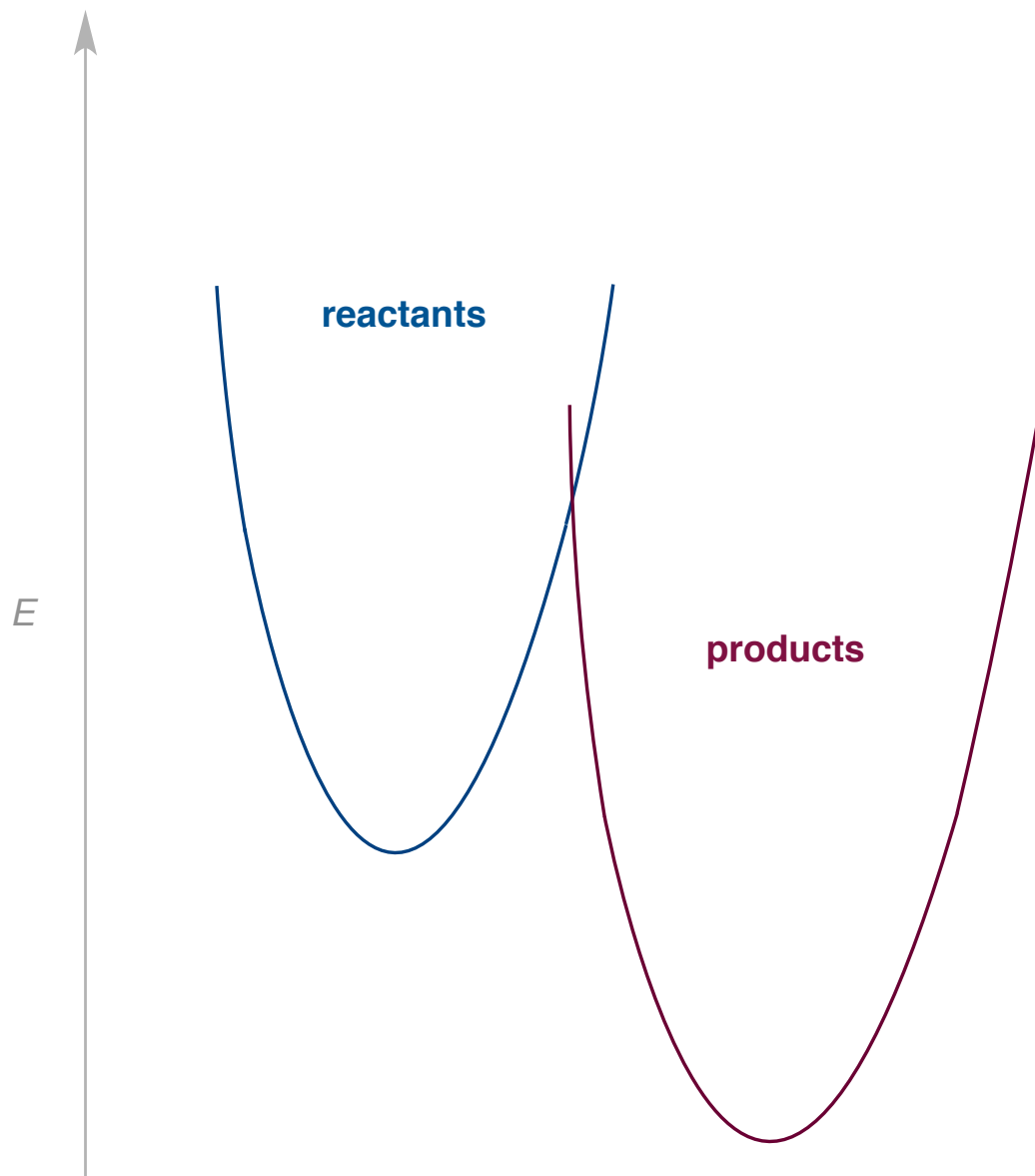
reaction coordinate



Breaking Down a Reaction Coordinate Diagram



Breaking Down a Reaction Coordinate Diagram



In Marcus theory:
potential energy wells can be
represented by parabolas

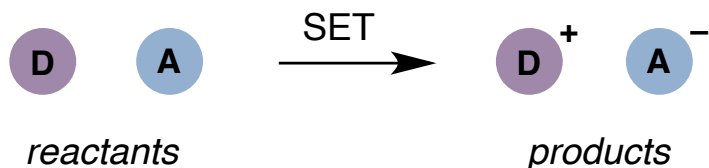


geometry of parabolas
can be used to calculate
kinetic barriers/reaction rates

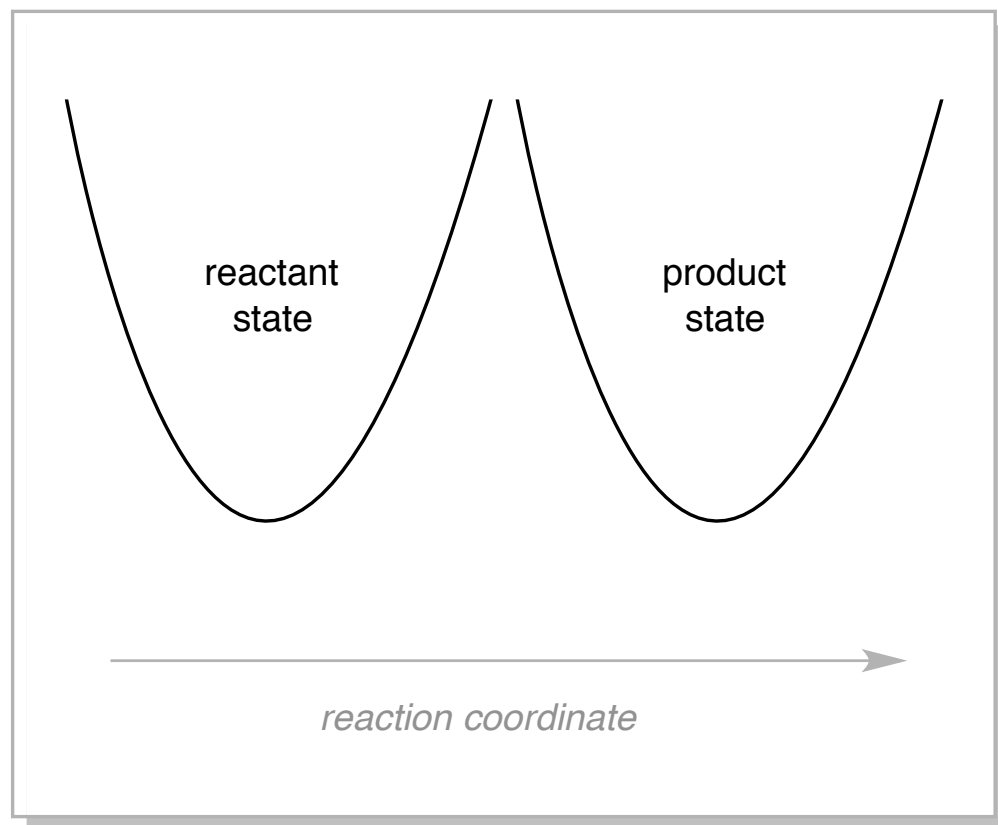
parabolic shape in region of interest

Basic Parabola Analysis: Single-Electron Transfer

■ Step 1: Draw parabolas for reactant and product states on the reaction coordinate



What is the "reaction coordinate?"

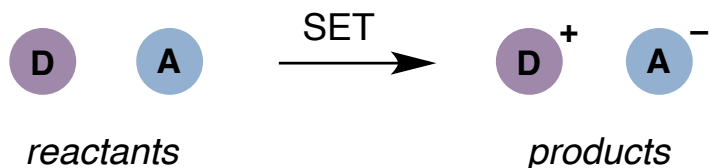


Reaction coordinate:
represents the nuclear coordinates
of the entire system undergoing the
reaction, including solvation

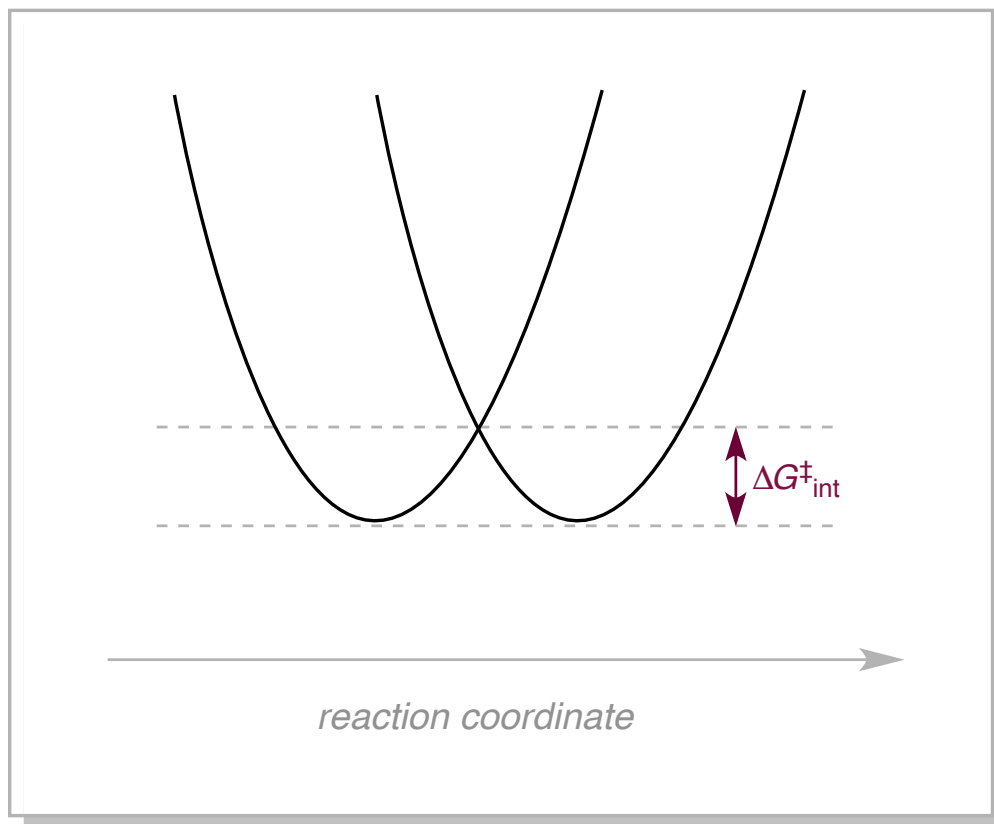
Nuclear coordinates:
indicate bond distances and angles
angles between and within reactants

Basic Parabola Analysis: Single-Electron Transfer

■ Step 1: Draw parabolas for reactant and product states on the reaction coordinate



How far apart do we place the parabolas?



Parabolas are placed such that their intersection lies at the "intrinsic barrier"

Intrinsic barrier, $\Delta G^\ddagger_{\text{int}}$:
barrier to hypothetical ergoneutral
reaction ($\Delta G^\circ = 0$); $\Delta G^\ddagger_{\text{int}} \approx \lambda/4$

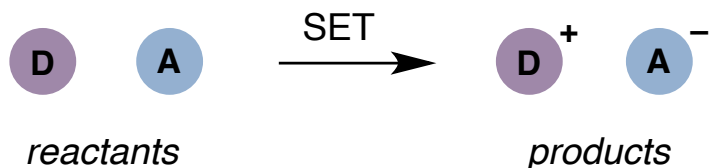
Reorganization energy, λ :
energy required to reorganize nuclei
without electron transfer occurring

Marcus, R. A. *J. Phys. Chem.* **1968**, 72, 891.

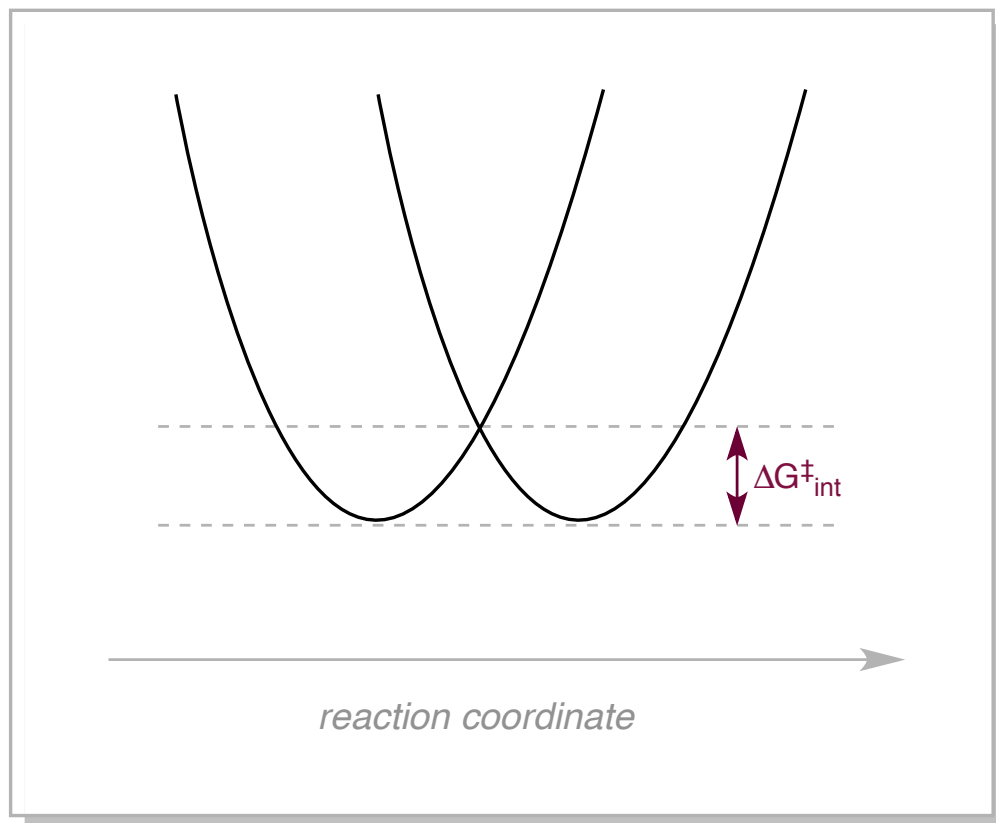
Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*, 1st ed.; University Science Books: Sausalito, 2006.

Basic Parabola Analysis: Single-Electron Transfer

■ Step 1: Draw parabolas for reactant and product states on the reaction coordinate

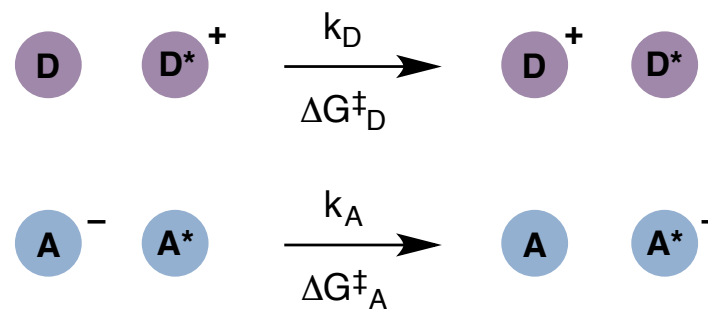


How is the intrinsic barrier determined?



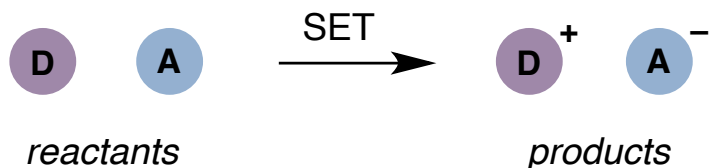
$$\Delta G^{\ddagger}_{\text{int}} = (\Delta G^{\ddagger}_{\text{D}} + \Delta G^{\ddagger}_{\text{A}})/2$$

intrinsic barrier is the average of the barriers to the self-exchange reactions

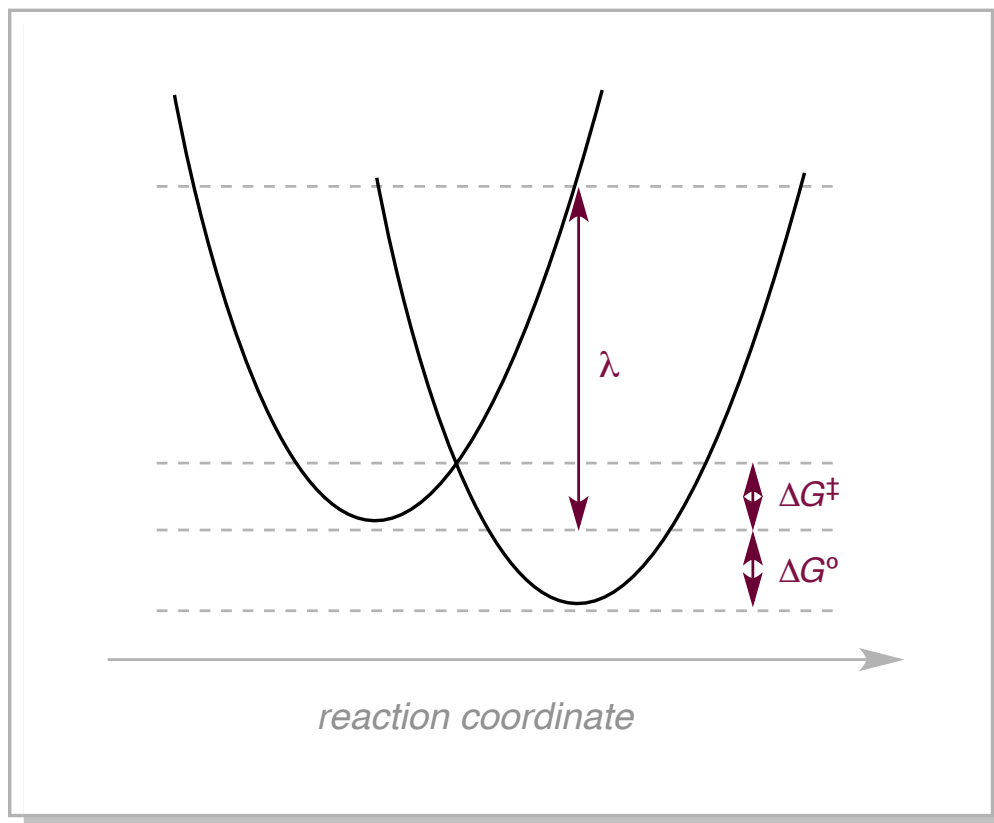


Basic Parabola Analysis: Single-Electron Transfer

■ Step 2: Incorporate thermodynamic parameters by adjusting parabola height



Change parabola height to reflect ΔG°



Exergonic reaction:

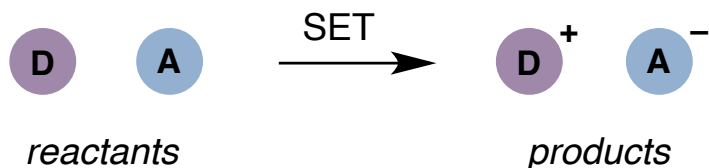
lower product parabola to reflect $\Delta G^\circ < 0$

Endergonic reaction:

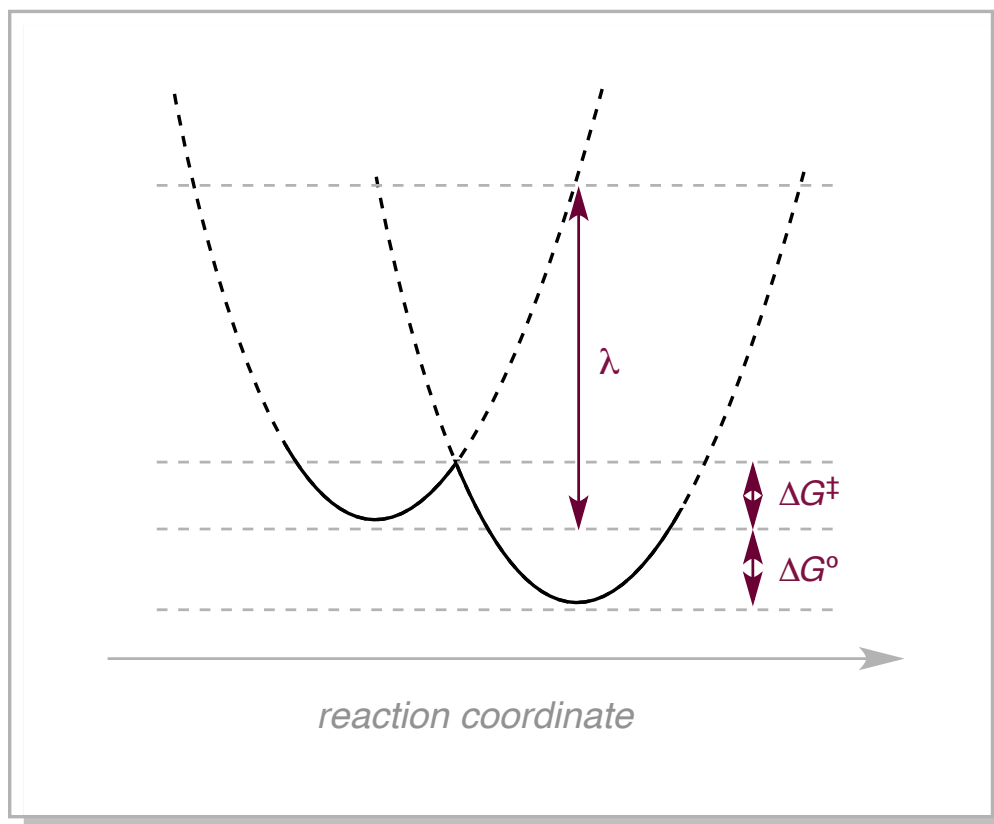
raise product parabola to reflect $\Delta G^\circ > 0$

Basic Parabola Analysis: Single-Electron Transfer

■ Step 3: Calculate values of interest: ΔG^\ddagger , rate, lateness/earliness of transition state



Overlapping parabolas map potential E curve



Calculation of kinetic barrier:
y-coordinate of point of intersection

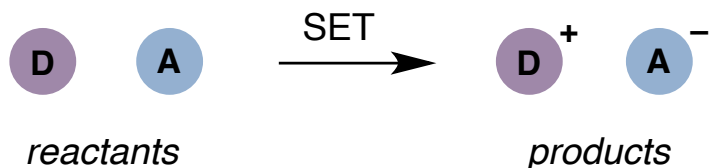
$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$$

Calculation of reaction rate:
using the Eyring equation

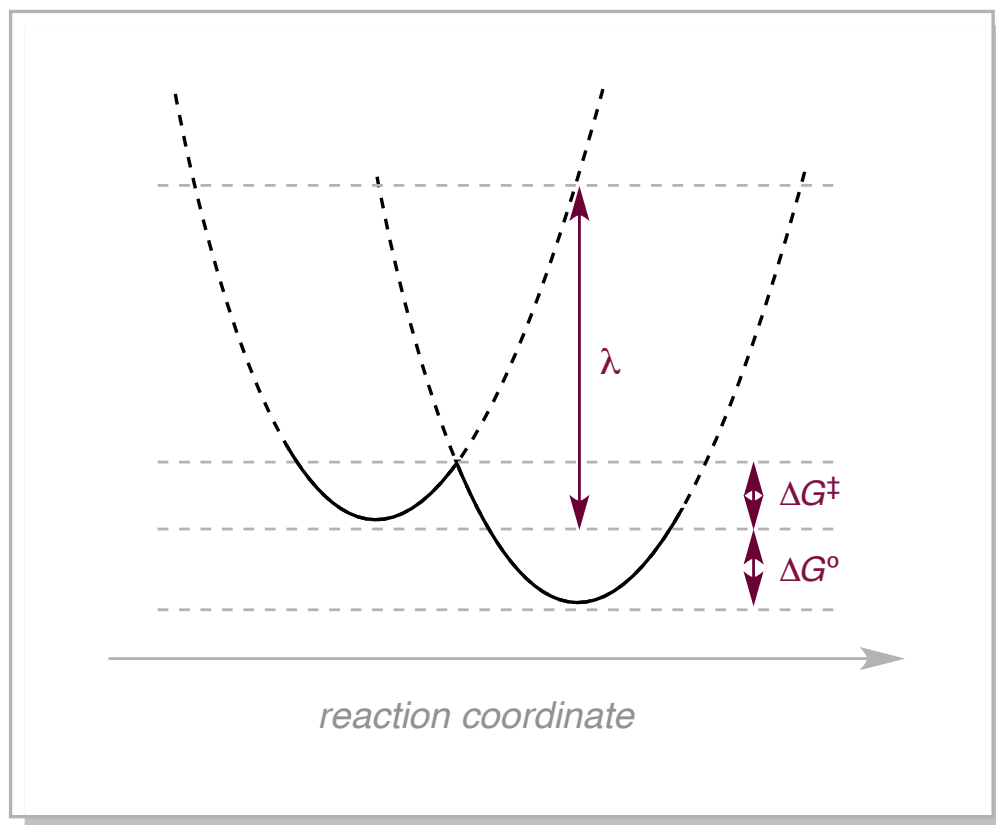
$$k_{ET} = \kappa \frac{k_B T}{h} \exp\left(\frac{-(\lambda + \Delta G^\circ)^2}{4\lambda RT}\right)$$

Basic Parabola Analysis: Single-Electron Transfer

■ Step 3: Calculate values of interest: ΔG^\ddagger , rate, lateness/earliness of transition state



Overlapping parabolas map potential E curve



Earliness/lateness of transition state:
x-coordinate of point of intersection

$$x^\ddagger = \frac{\lambda + \Delta G^\circ}{(2k\lambda)^{1/2}}$$

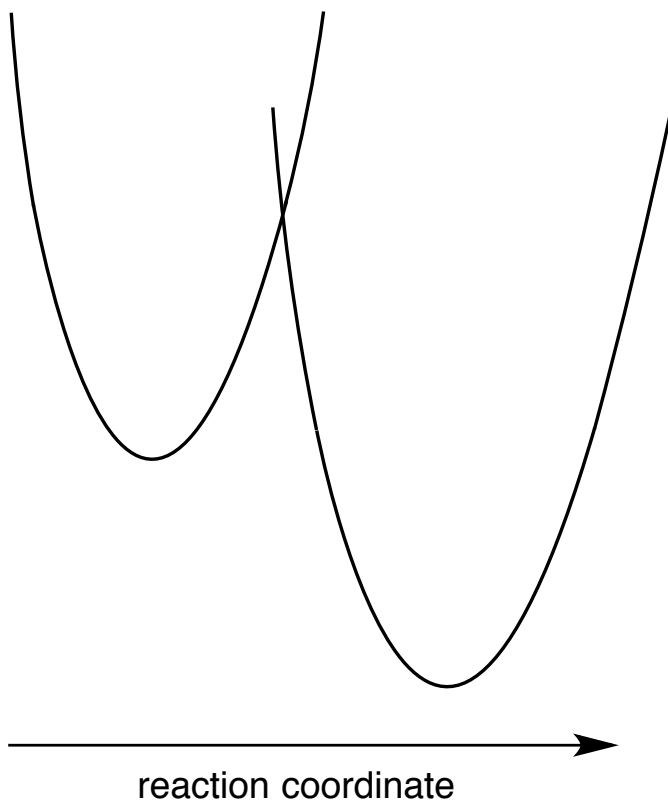
where k = composite force constant

Adiabaticity: Smoothing out the Potential Energy Surface

Non-adiabatic electron transfer

Nuclei do not move during electron transfer, jump between states required

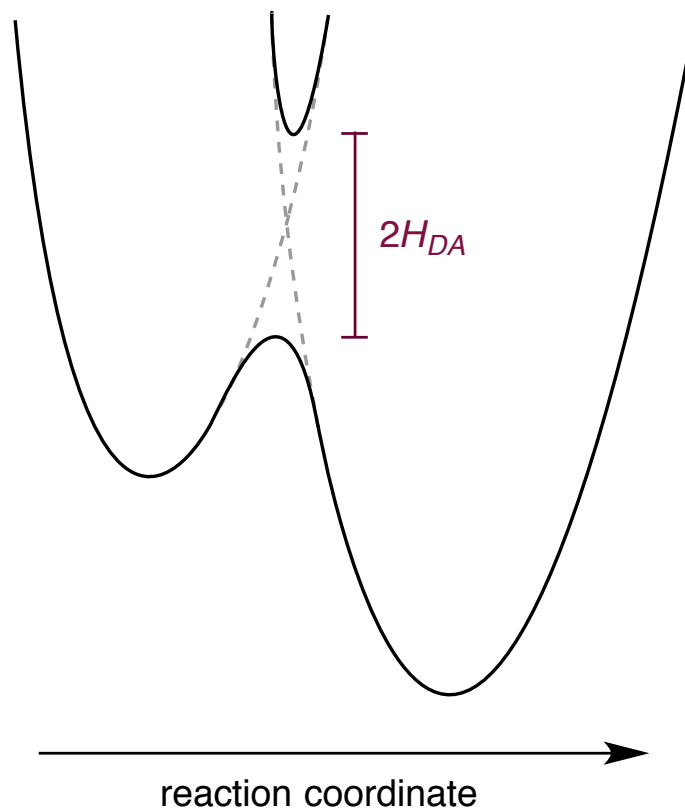
H_{DA} = electronic coupling = small



Adiabatic electron transfer

Nuclear motion is coupled to electron motion, system remains on one surface

H_{DA} = electronic coupling = large



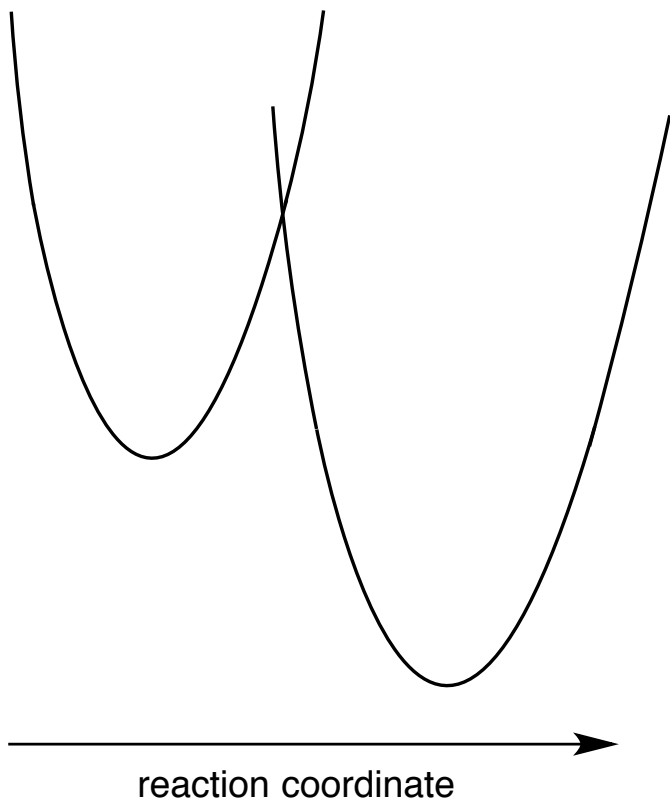
Adiabaticity: Smoothing out the Potential Energy Surface

Non-adiabatic electron transfer

Recall: $k_{ET} \propto \kappa$

For non-adiabatic ET: $\kappa \propto (H_{DA})^2$

$H_{DA} = \text{small} \Rightarrow \kappa \ll 1$

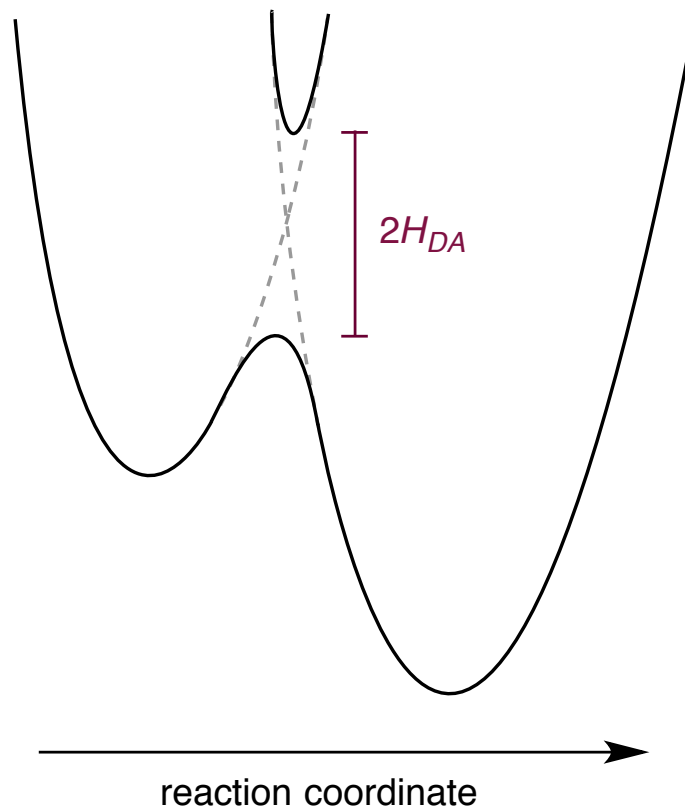


Adiabatic electron transfer

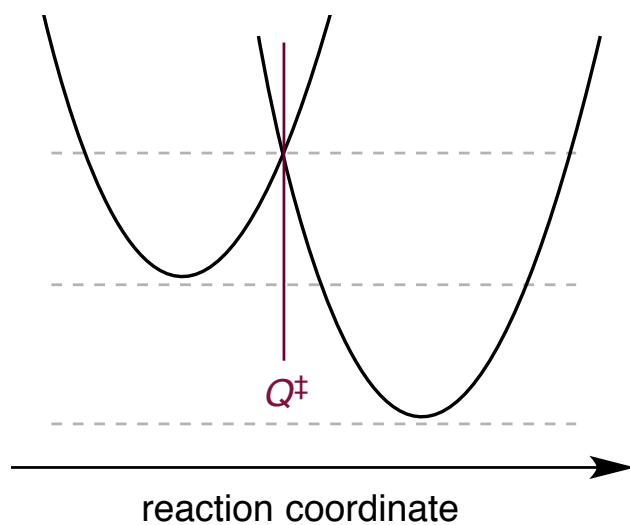
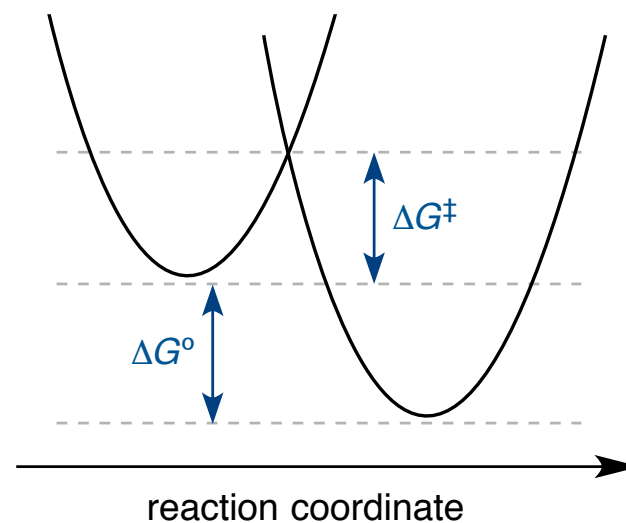
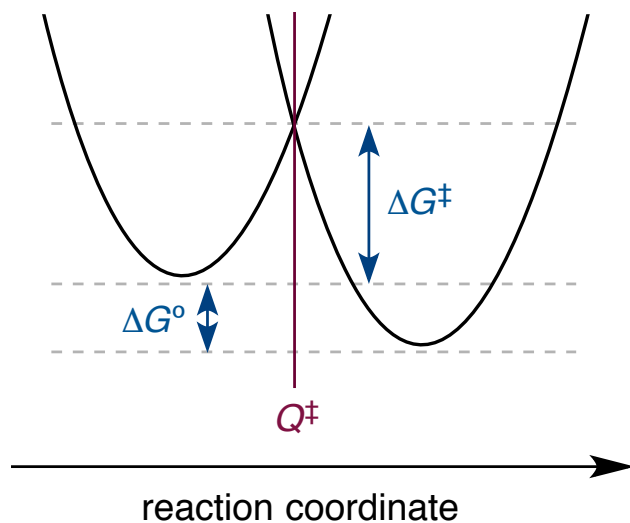
Recall: $k_{ET} \propto \kappa$

For adiabatic ET: $\kappa \approx 1$

$H_{DA} = \text{large} \Rightarrow \kappa \approx 1$



The Effect of Thermodynamics on the Kinetic Barrier

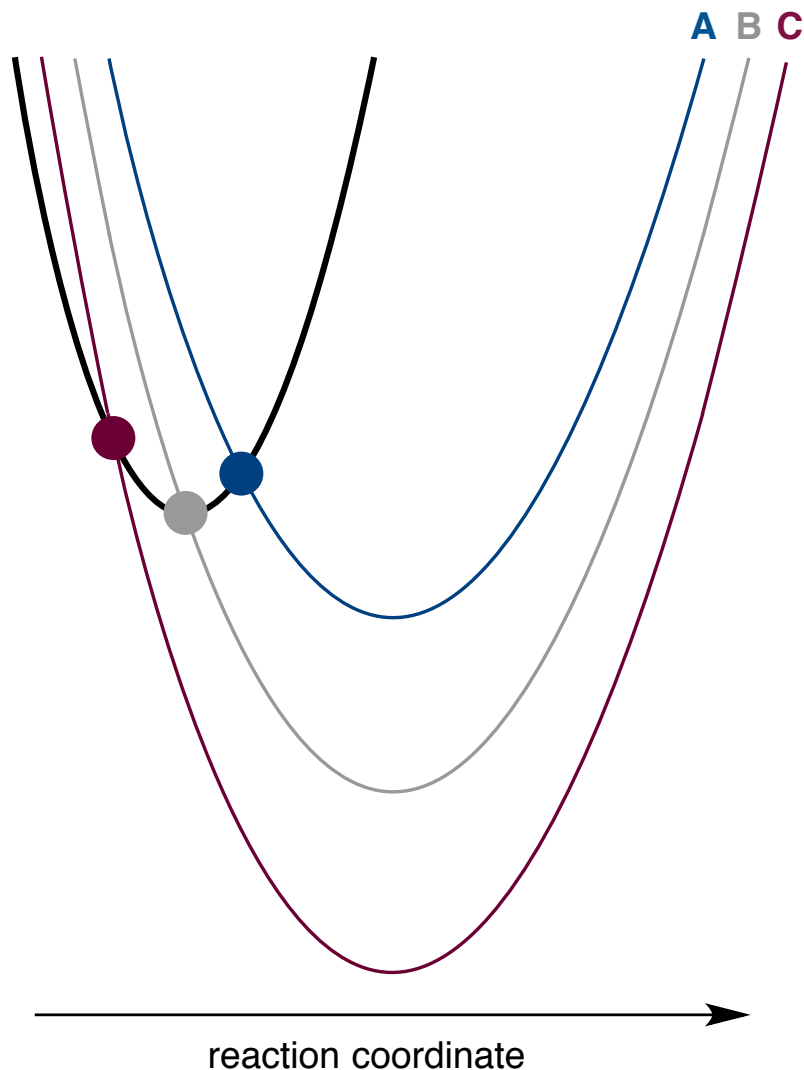


*More exothermic reactions tend to be faster,
more endothermic reactions tend to be slower*

*Exothermic reactions tend to have early TS,
endothermic reactions tend to have late TS
(the Hammond postulate)*

Prediction of the Marcus Inverted Region

Consider a series of exothermic reactions:



A $\Delta G^\circ < 0$ (somewhat negative)

● $\Delta G^\ddagger > 0$, rate k_A

B $\Delta G^\circ = -\lambda$ (quite negative)

● $\Delta G^\ddagger = 0$, rate $k_B > k_A$

C $\Delta G^\circ \ll 0$ (very negative)

● $\Delta G^\ddagger > 0$, rate $k_C < k_B$

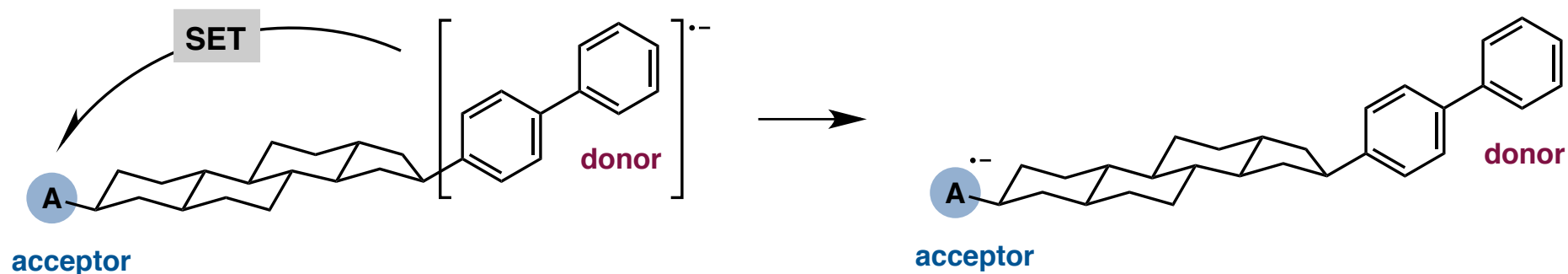
As ΔG° approaches $-\lambda$, the rate of reaction *increases*

When $\Delta G^\circ = -\lambda$, the reaction becomes barrierless

As ΔG° becomes even more negative ($\Delta G^\circ < -\lambda$),
the rate of reaction *decreases* ($\Delta G^\ddagger > 0$)

Marcus inverted region

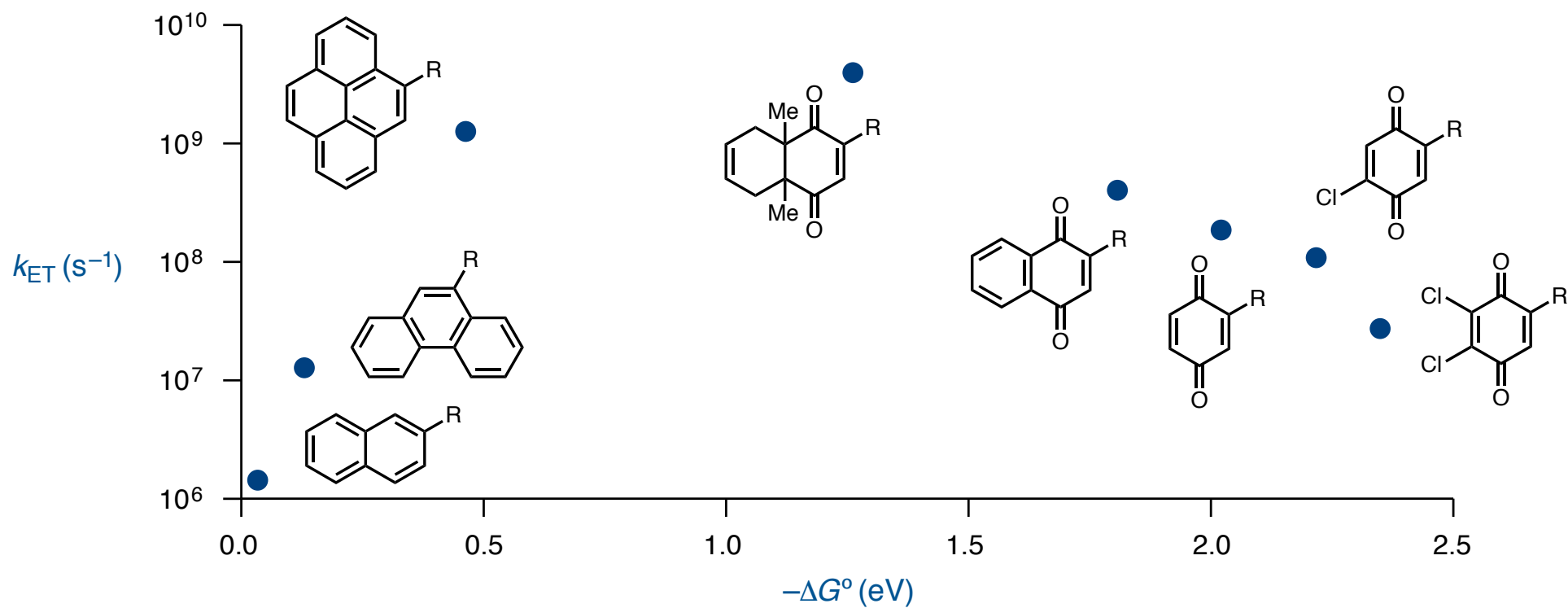
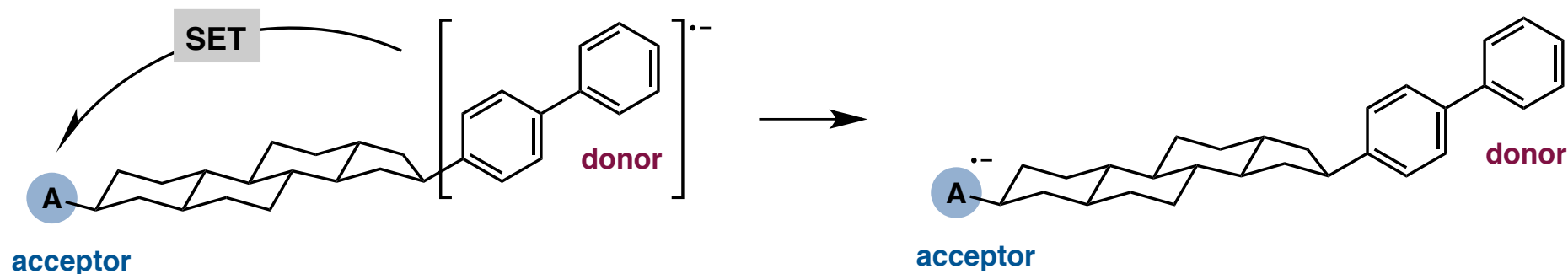
Confirmation of the Marcus Inverted Region



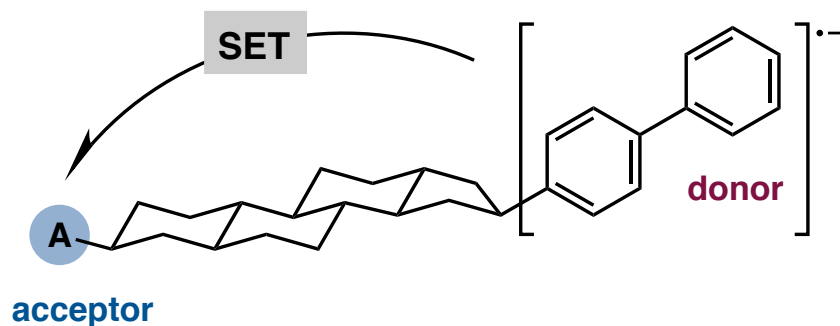
Closs and Miller, 1984

pulse radiolysis study of *intramolecular*
 e^- transfer between an electron donor
and a range of electron acceptors

Confirmation of the Marcus Inverted Region



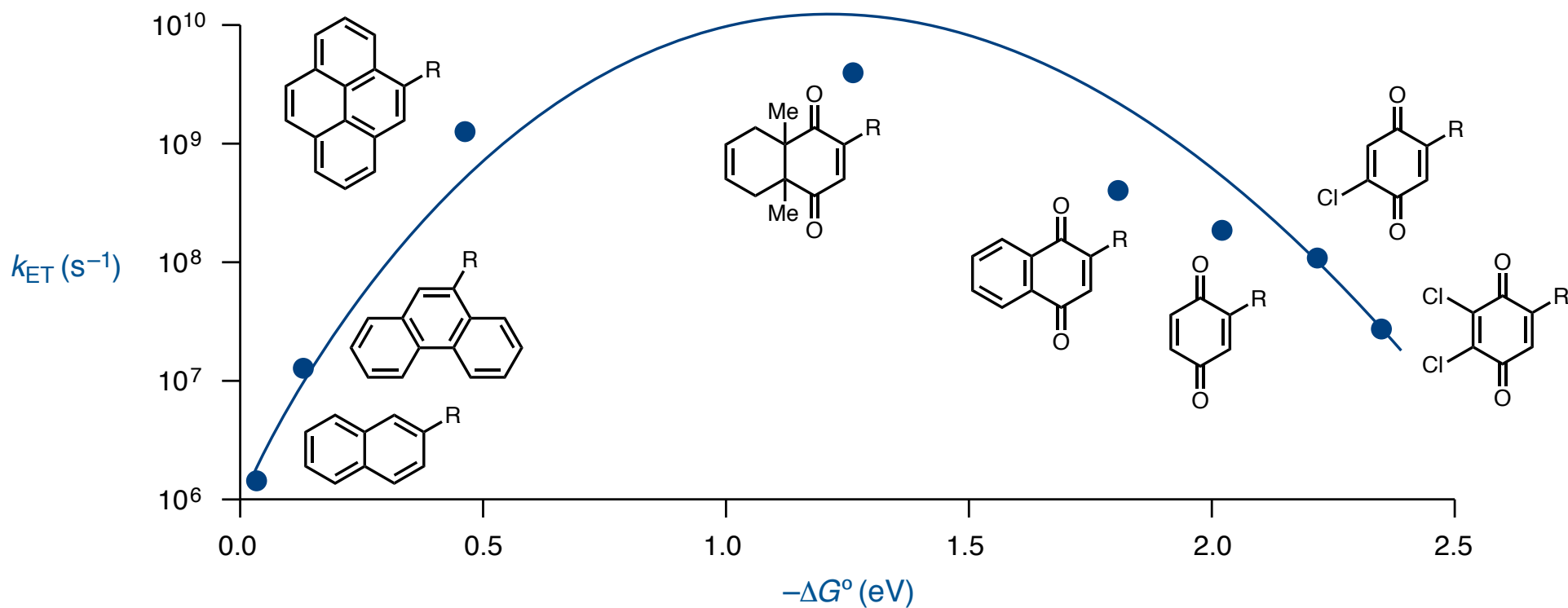
Confirmation of the Marcus Inverted Region



Closs and Miller, 1984

more negative ΔG° produces increase in rate, then decrease in rate after maximum:

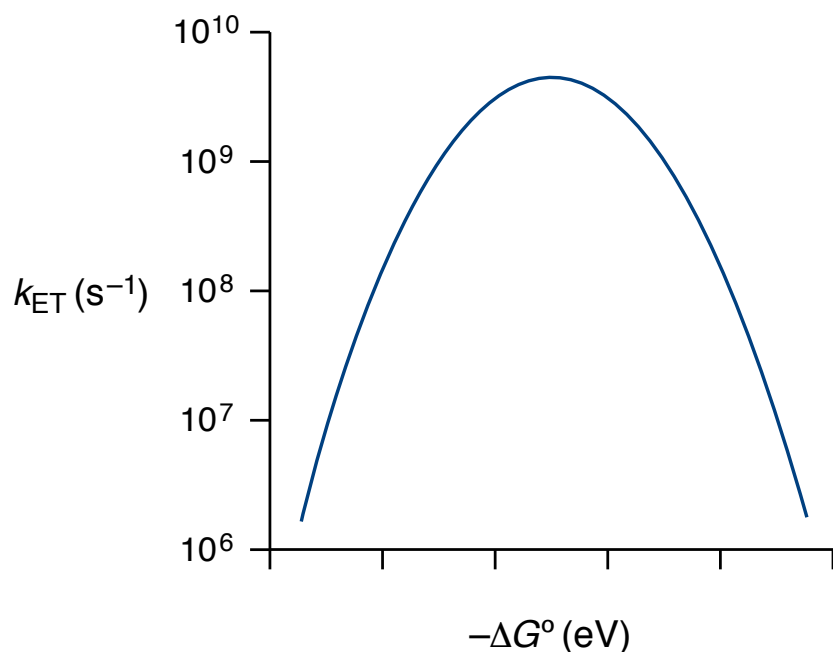
evidence for the Marcus inverted region



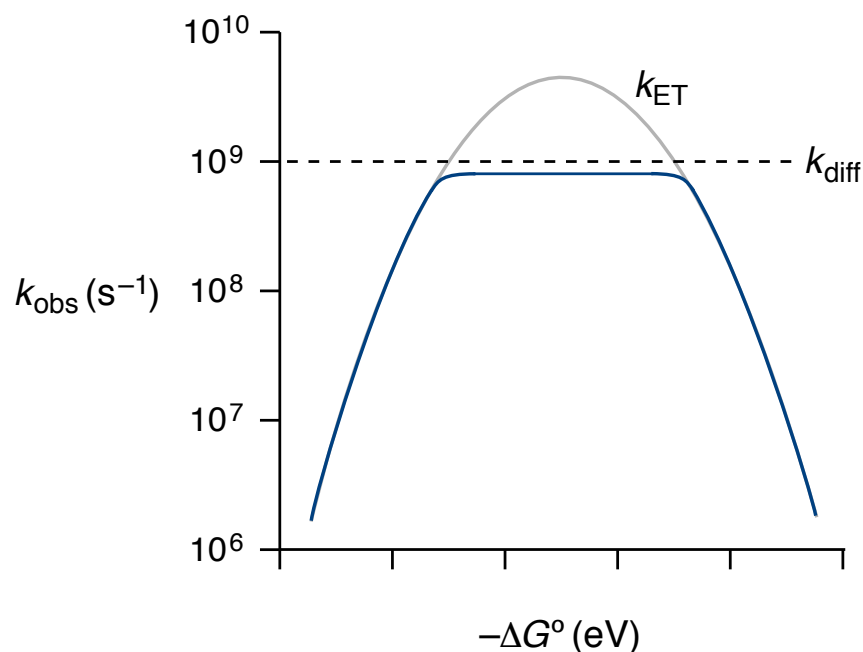
Confirmation of the Marcus Inverted Region

Why did it take almost 30 years to verify the existence of the Marcus inverted region?

Intramolecular electron transfer
(e.g., Closs and Miller)



Intermolecular electron transfer
(most ET reactions studied)



- 1. For intermolecular ET, observed rate is limited by diffusion ($k_{obs} = k_{diff}$ when $k_{ET} \gg k_{diff}$)**
- 2. To escape the diffusion "leveling effect," ΔG° must be very, very negative (difficult to achieve)**

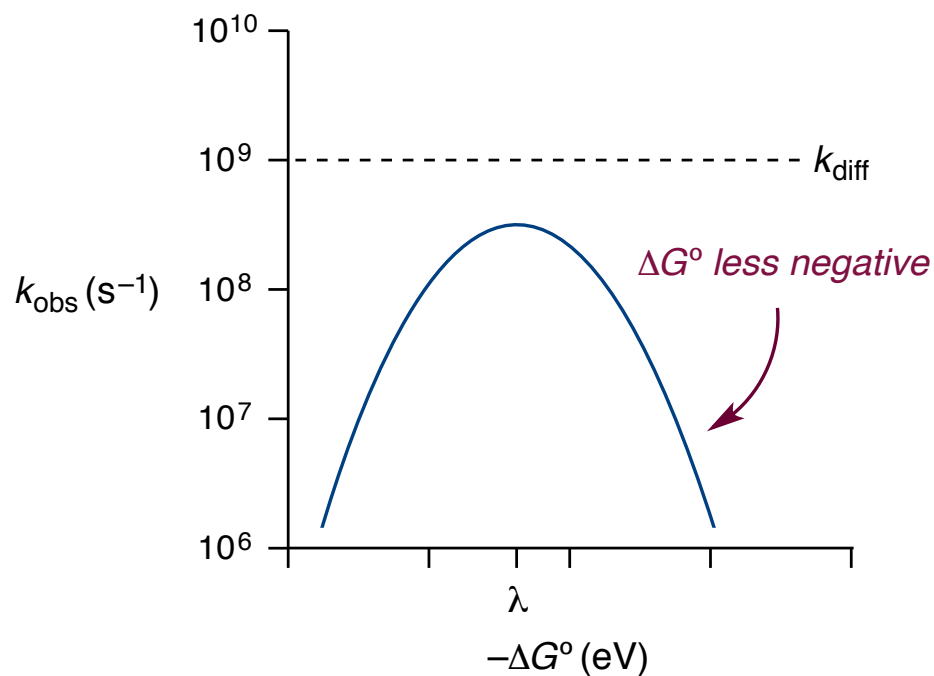
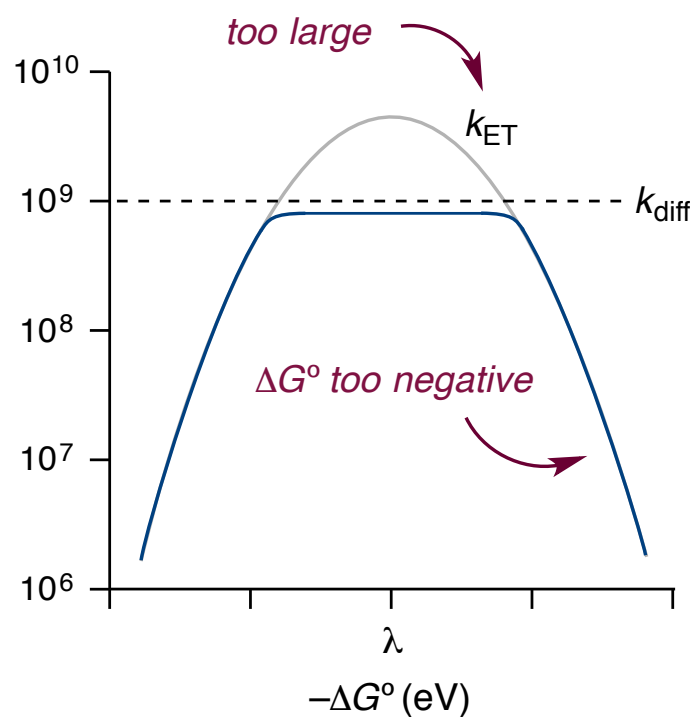
Inverted Behavior in Bimolecular Electron Transfer

1.

$$k_{\text{obs}} = \frac{k_{\text{ET}} k_{\text{diff}}}{k_{\text{ET}} + k_{\text{diff}}} \implies k_{\text{obs}} = k_{\text{diff}} \text{ for } k_{\text{ET}} \gg k_{\text{diff}}$$

2.

$-\Delta G^\circ$ must be $\gg \lambda$
to escape diffusion leveling



How might we adjust the thermodynamic/kinetic parameters to make the inverted region observable?

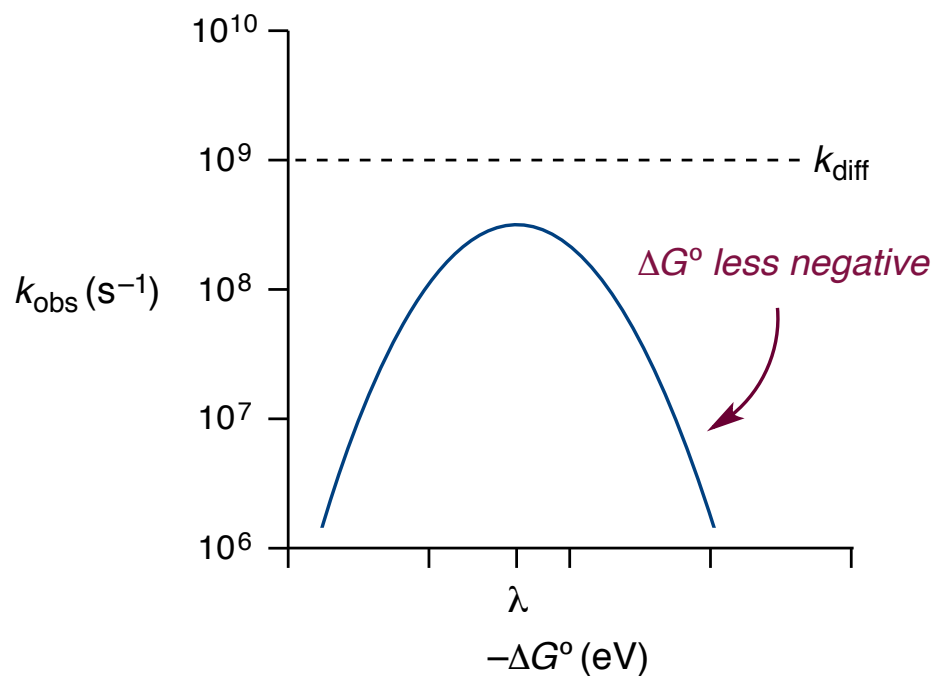
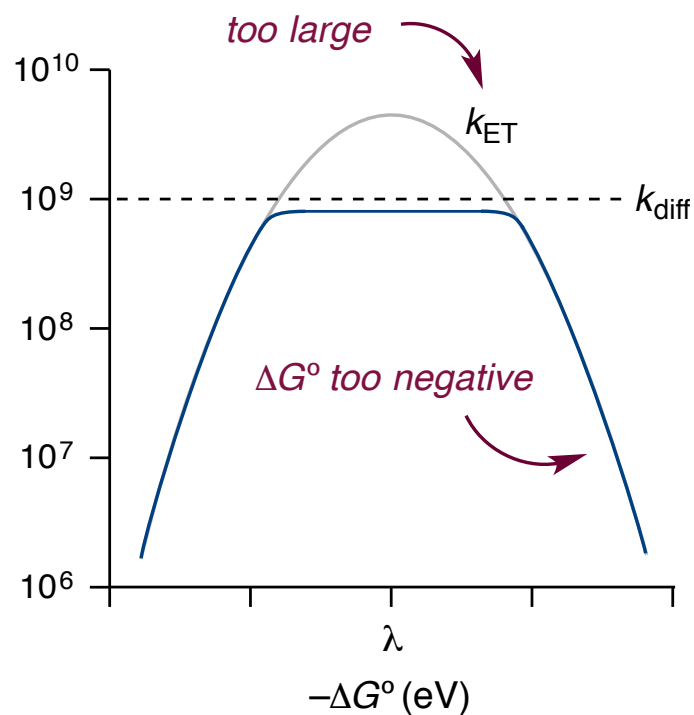
Inverted Behavior in Bimolecular Electron Transfer

1.

$$k_{\text{obs}} = \frac{k_{\text{ET}} k_{\text{diff}}}{k_{\text{ET}} + k_{\text{diff}}} \quad \Rightarrow \quad k_{\text{obs}} = k_{\text{diff}} \quad \text{for } k_{\text{ET}} \gg k_{\text{diff}}$$

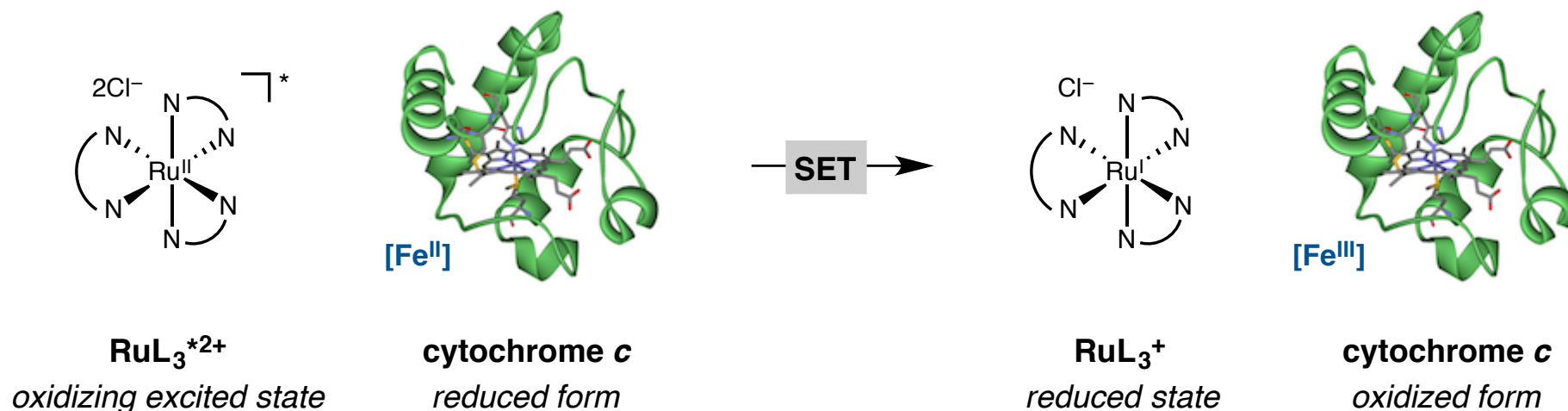
2.

$-\Delta G^\circ$ must be $\gg \lambda$
to escape diffusion leveling



Select a system with modest reorganization energy and driving force

Inverted Behavior in Bimolecular Electron Transfer



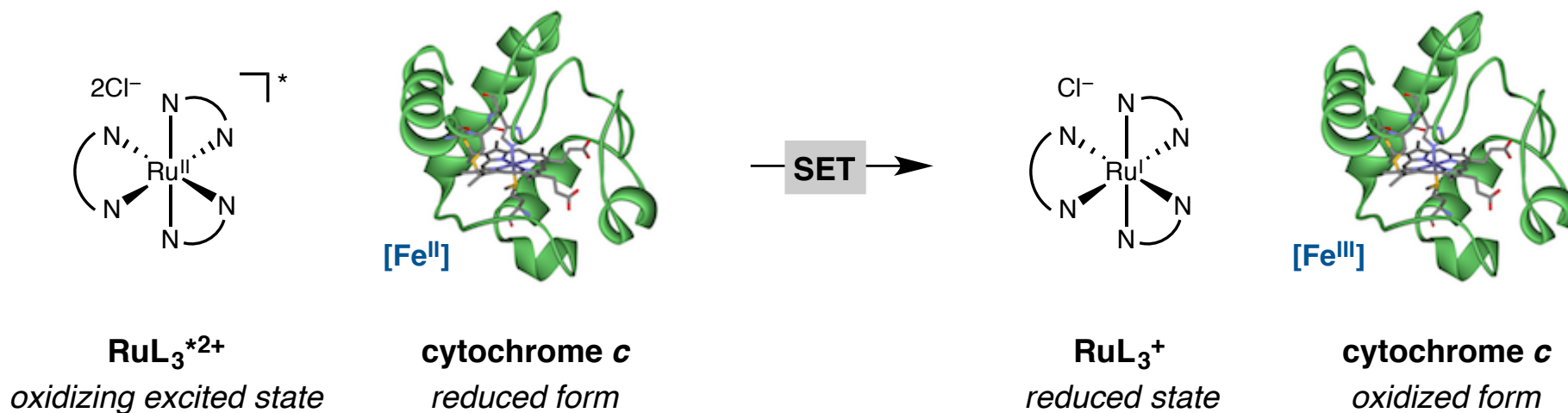
Cytochrome c

*moderate reorganization energy mostly due to solvation effects,
known to exhibit inverted region kinetics at $\Delta G^\circ \approx -1$ V in fixed-distance ET*

RuL₃*²⁺

reduction potentials well-matched for SET with cytochrome c to provide $\Delta G^\circ \approx -1$ V

Inverted Behavior in Bimolecular Electron Transfer



Ru ^{II} complex	$-\Delta G^\circ$	k_{obs} (M ⁻¹ s ⁻¹)
Ru(dOMephen) ₃ ²⁺	0.69 V	5.68×10^8
Ru(dMephen) ₃ ²⁺	0.40 V	2.84×10^8
Ru(phen) ₃ ²⁺	0.52 V	4.36×10^8
Ru(dCF ₃ bpy) ₃ ²⁺	1.32 V	3.11×10^8

diffusion limit = $k_{\text{diff}} = 8.8 \times 10^8$

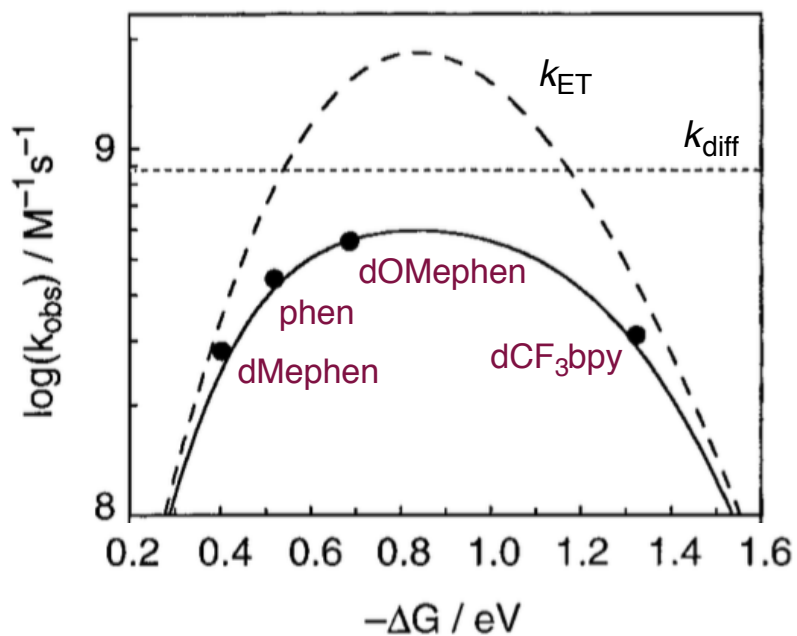
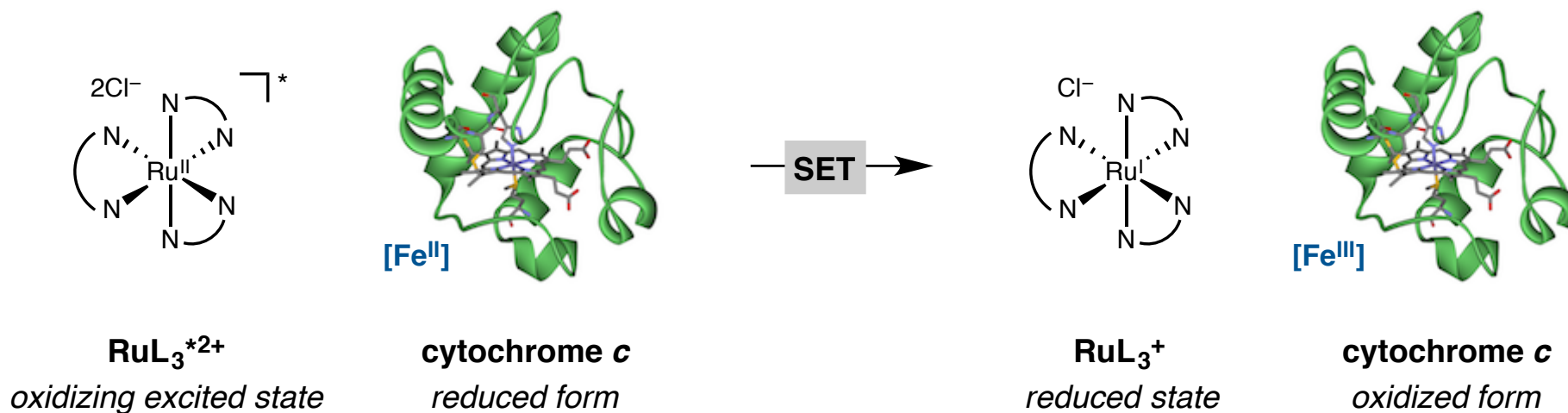


$k_{\text{obs}} < k_{\text{diff}}$ in all cases



inverted region should be apparent

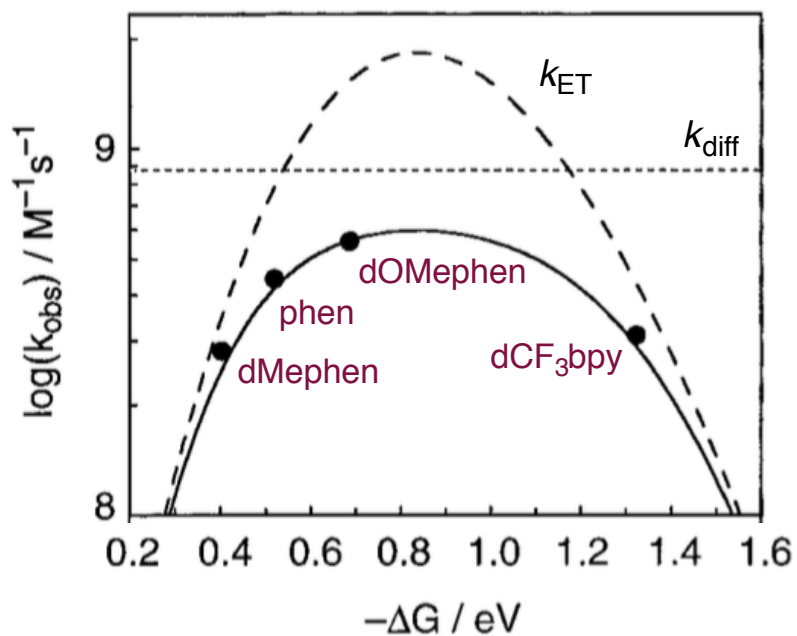
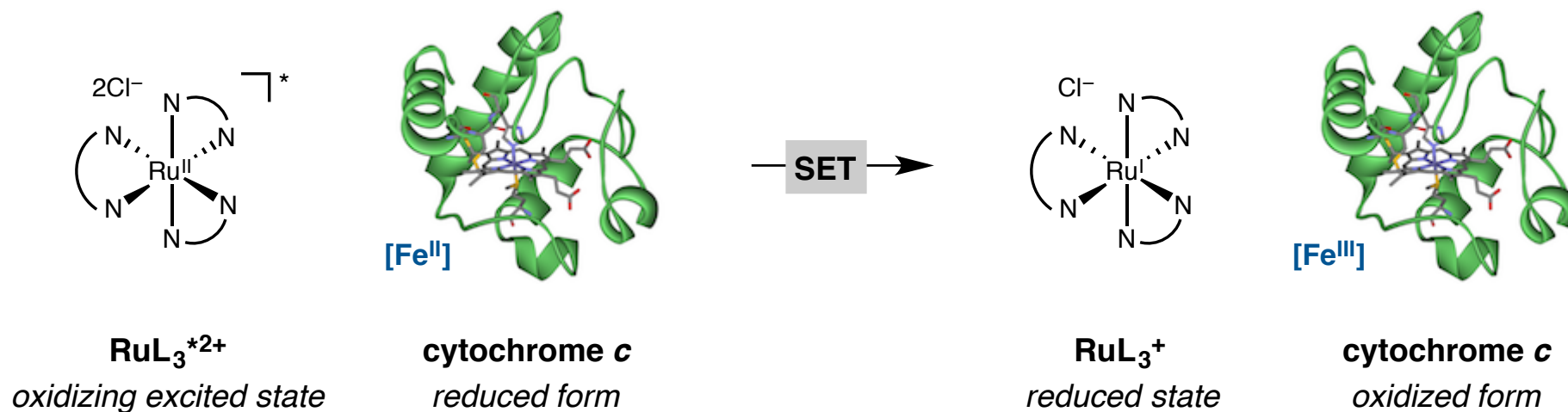
Inverted Behavior in Bimolecular Electron Transfer



Indeed, inverted behavior is observed

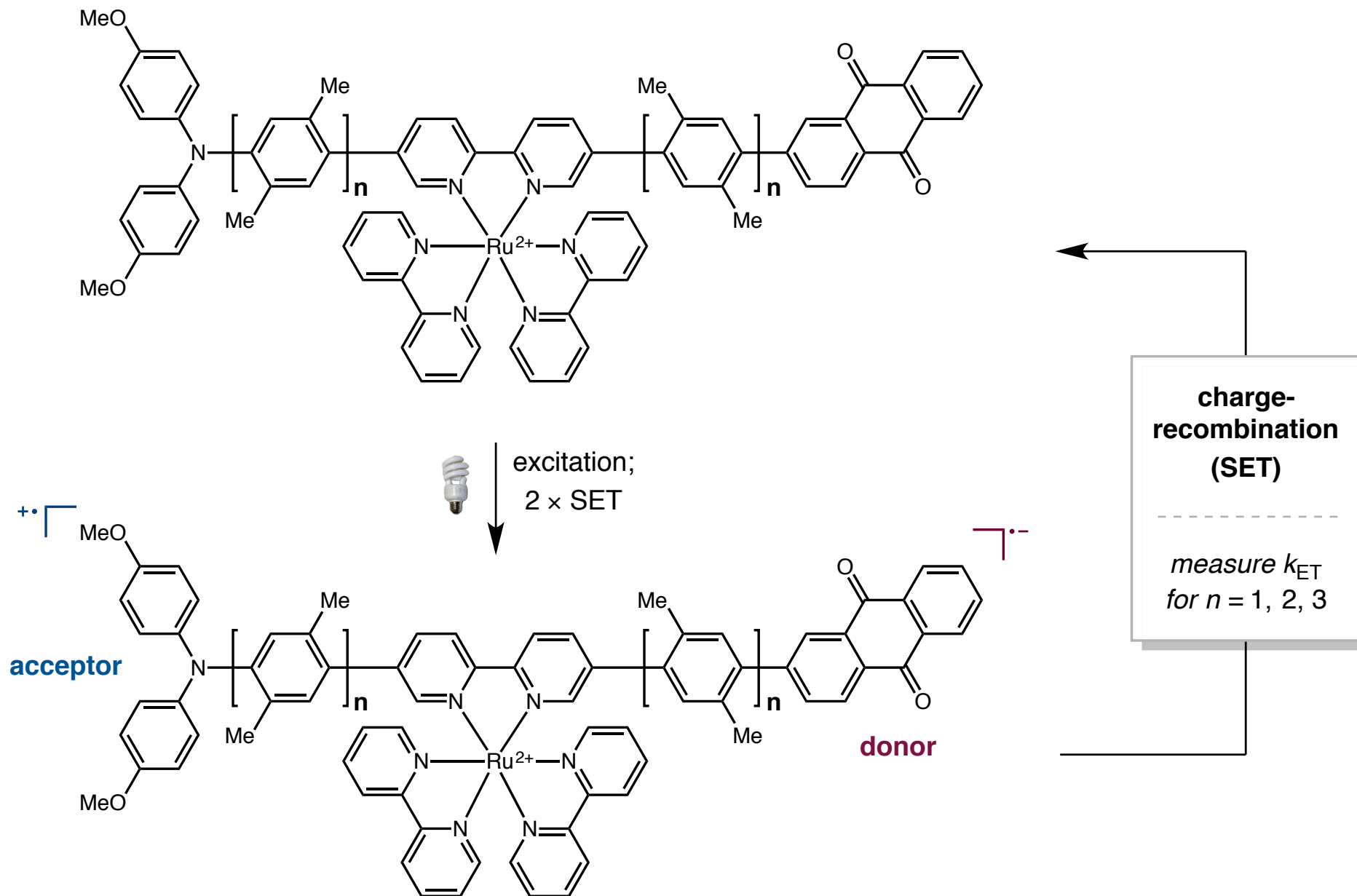
*flattening of curve is apparent
due to contribution of k_{diff}*

Inverted Behavior in Bimolecular Electron Transfer

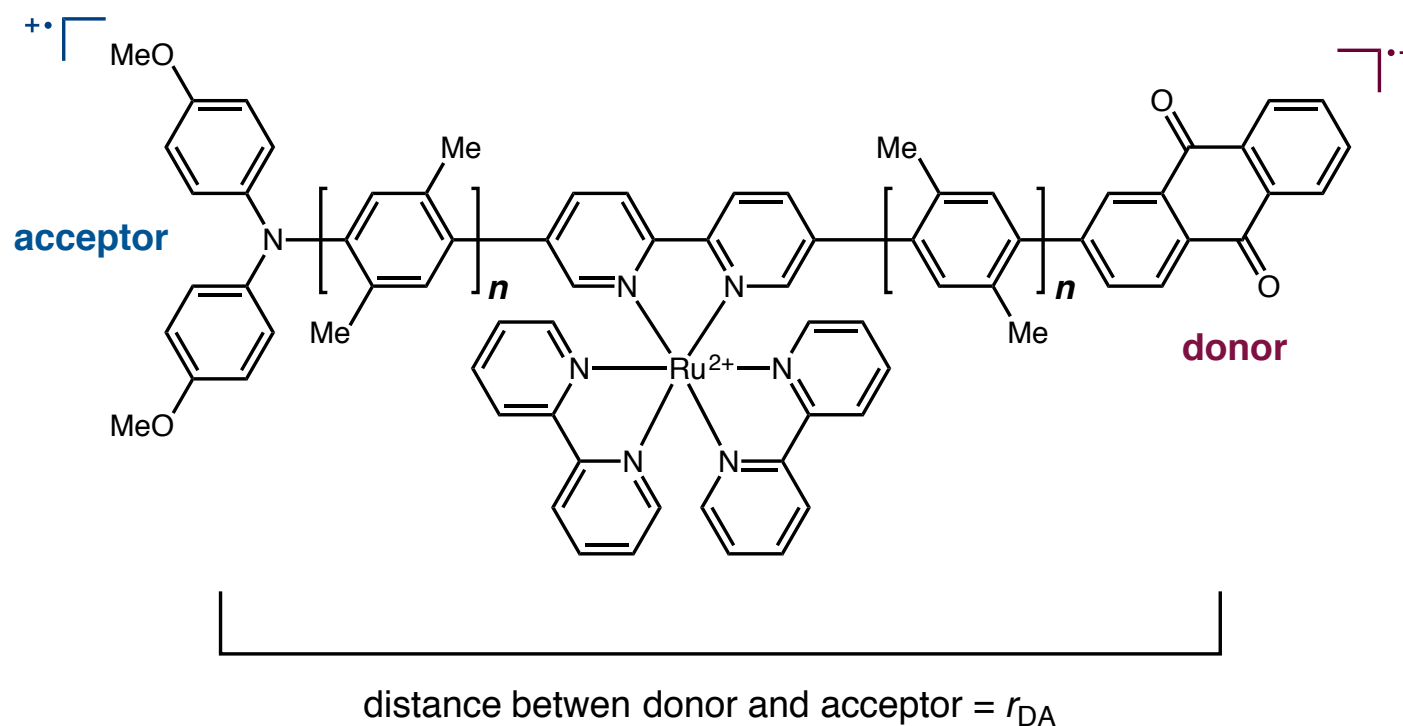


Rational tuning of thermodynamic and kinetic parameters allows provides desired electron transfer behavior

The Influence of Donor-Acceptor Distance on Electron Transfer Rates



The Influence of Donor-Acceptor Distance on Electron Transfer Rates

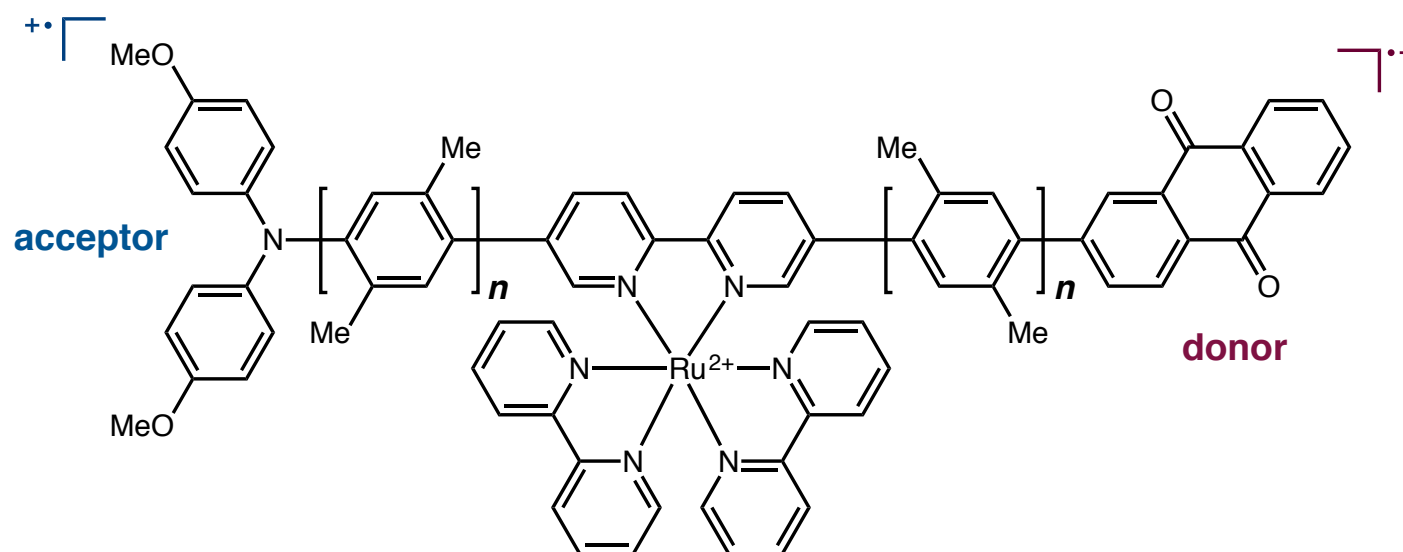


$$n = 1 : r_{DA} = 22.0 \text{ \AA}$$

$$n = 2 : r_{DA} = 30.6 \text{ \AA}$$

$$n = 3 : r_{DA} = 39.2 \text{ \AA}$$

The Influence of Donor-Acceptor Distance on Electron Transfer Rates

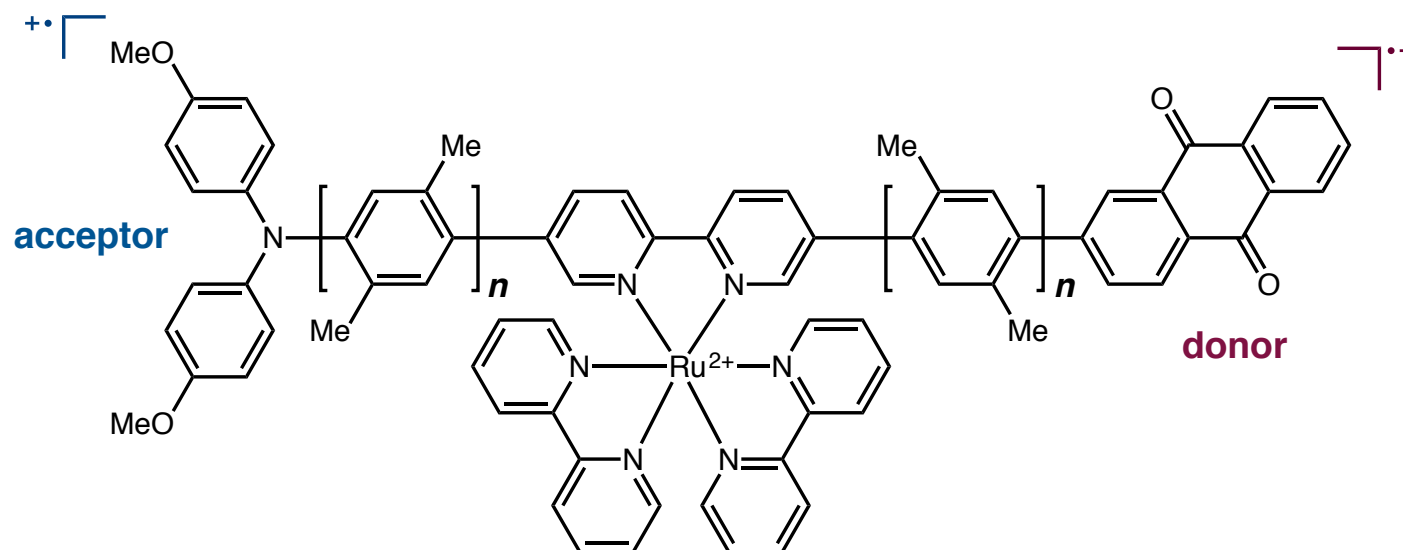


Calculation of ΔG° from reduction potentials

	$E_{1/2}^{\text{red}}(\text{D}^+/\text{D})$	$E_{1/2}^{\text{red}}(\text{A}/\text{A}^-)$	$-\Delta G^\circ$
$n = 1$	0.63 V	-0.70 V	1.33 V
$n = 2$	0.59 V	-0.70 V	1.29 V
$n = 3$	0.58 V	-0.65 V	1.23 V

Linker length does not significantly effect the thermodynamic driving force

The Influence of Donor-Acceptor Distance on Electron Transfer Rates



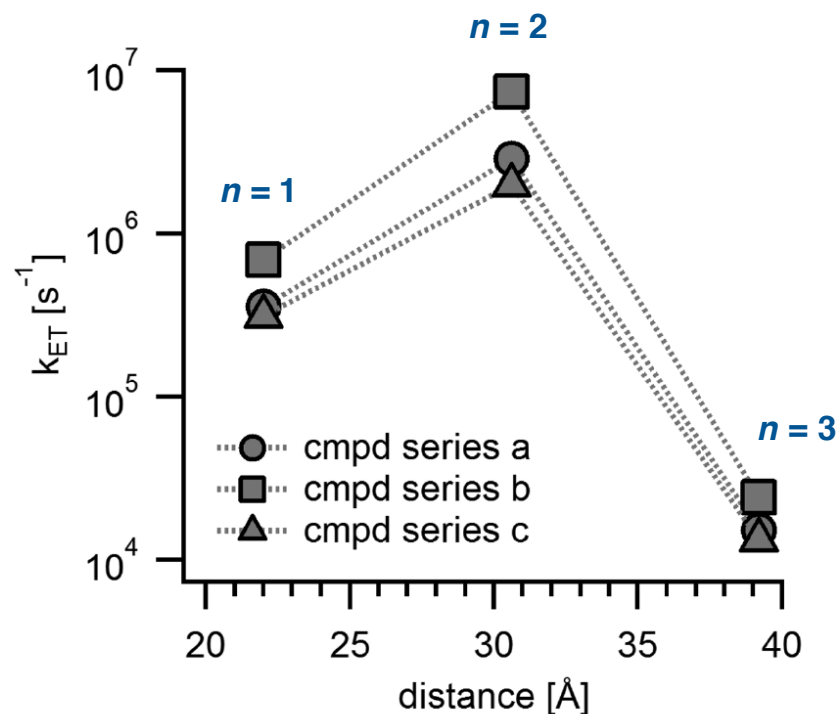
Linker length does not significantly affect the thermodynamic driving force

We have previously seen that ΔG^0 can control the rate of reaction



If ΔG° controls the rate of reaction, k_{ET} should be very similar for $n = 1, 2, 3$

The Influence of Donor-Acceptor Distance on Electron Transfer Rates



linker length changes k_{ET}
by 1 to 2 orders of magnitude



parameters other than ΔG°
influence the reaction rate

We have previously seen that ΔG° can control the rate of reaction



If ΔG° controls the rate of reaction, k_{ET} should be very similar for $n = 1, 2, 3$

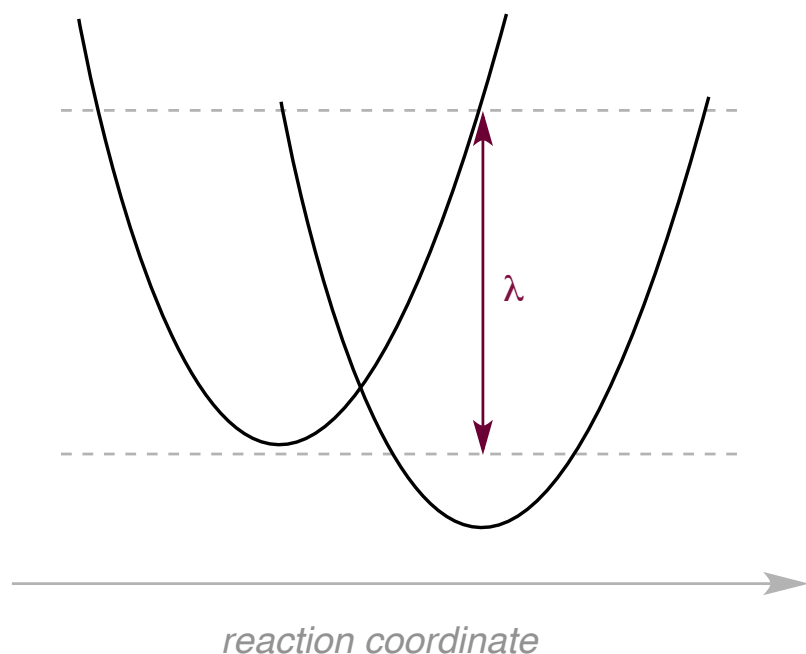
The Influence of Donor-Acceptor Distance on Electron Transfer Rates

Recall:

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

$$k_{ET} = \kappa \frac{k_B T}{h} \exp\left(\frac{-(\lambda + \Delta G^\circ)^2}{4\lambda RT}\right)$$

What about this mysterious " λ " parameter?



λ = reorganization energy

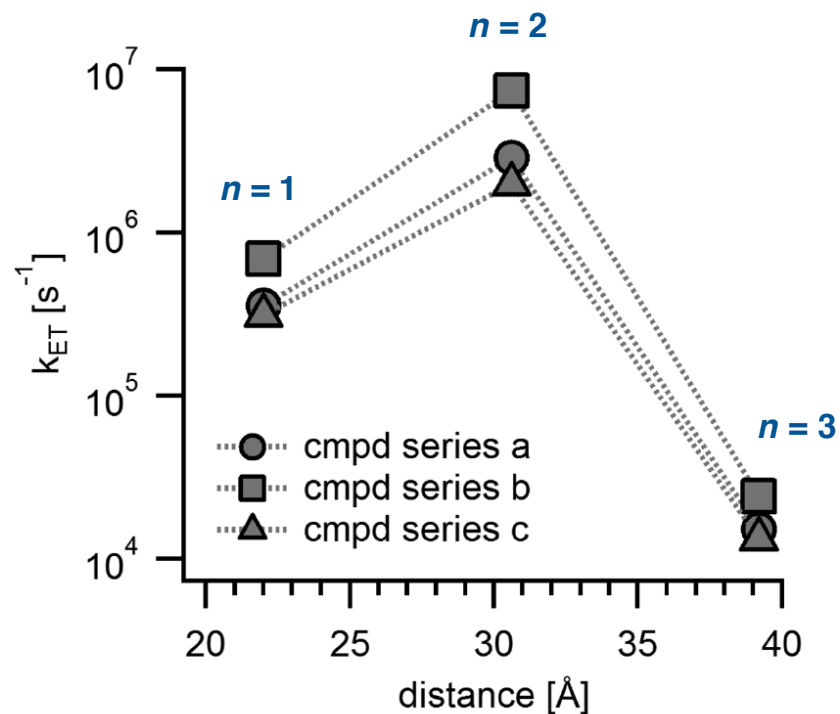
= energy required to reorganize nuclei from coordinates of reactant state to coordinates of product state, including reorganization of relevant solvent molecules



for charge separation over long distance, significant solvent reorganization should be expected

λ should increase as r_{DA} increases

The Influence of Donor-Acceptor Distance on Electron Transfer Rates

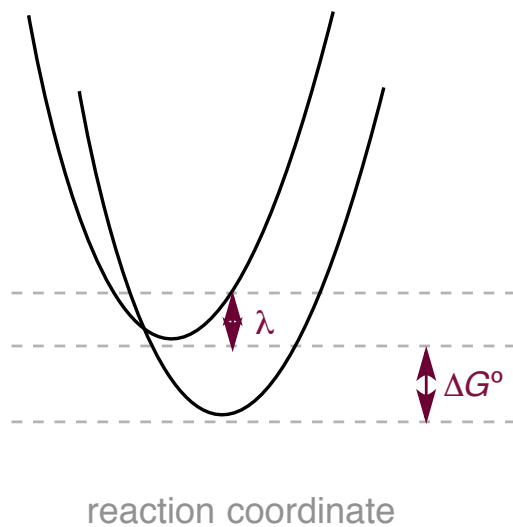


Why does k_{ET} increase from $n = 1$ to $n = 2$?

(Shouldn't increasing r_{DA} slow down the reaction?)

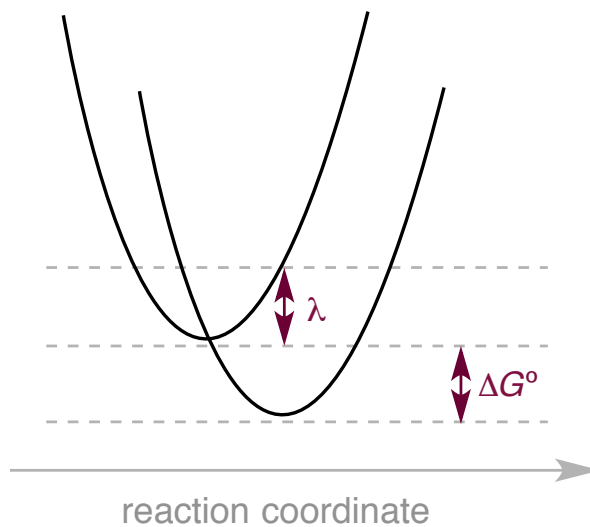
The Influence of Donor-Acceptor Distance on Electron Transfer Rates

$n = 1$, $r_{\text{DA}} = \text{small}$
inverted region



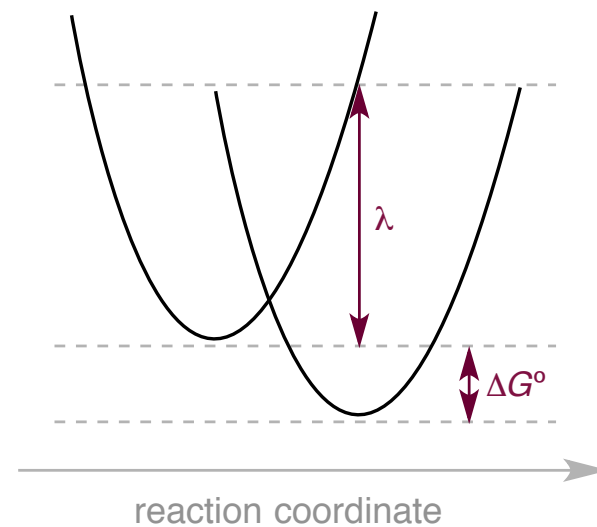
$$k_{\text{ET}} = 3.58 \times 10^5 \text{ s}^{-1}$$
$$\Delta G^\ddagger = 43 \text{ meV}$$

$n = 2$, $r_{\text{DA}} = \text{intermediate}$
barrierless reaction



$$k_{\text{ET}} = 2.87 \times 10^6 \text{ s}^{-1}$$
$$\Delta G^\ddagger = -2 \text{ meV}$$

$n = 3$, $r_{\text{DA}} = \text{large}$
normal region



$$k_{\text{ET}} = 1.53 \times 10^4 \text{ s}^{-1}$$
$$\Delta G^\ddagger = 126 \text{ meV}$$

The Influence of Donor-Acceptor Distance on Electron Transfer Rates

In the inverted region, k_{ET} increases with increasing distance between donor and acceptor

Implications for solar energy conversion (and other applications?)

For efficient solar energy conversion:

photoinduced ET must be fast, thermal charge recombination must be slow

Challenges:

- 1. photoinduced ET generally occurs in the normal region
(donor and acceptor must be close together for efficient ET)*
- 2. thermal charge recombination generally occurs in the inverted region
(rate of ET increases as donor and acceptor diffuse, until they reach critical r_{DA})*