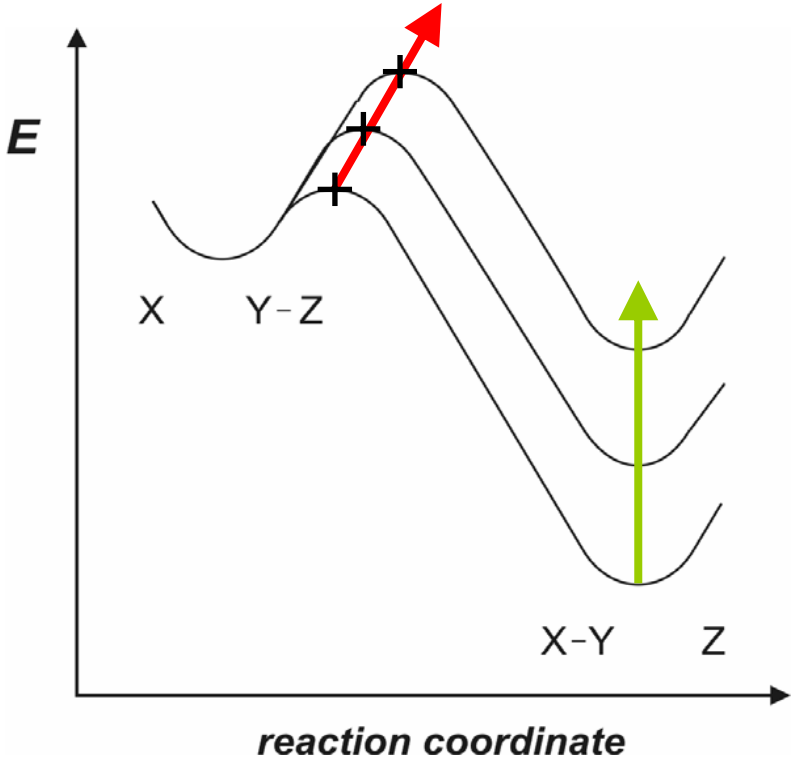
Kinetic-Thermodynamic Connections: Hammond Postulate



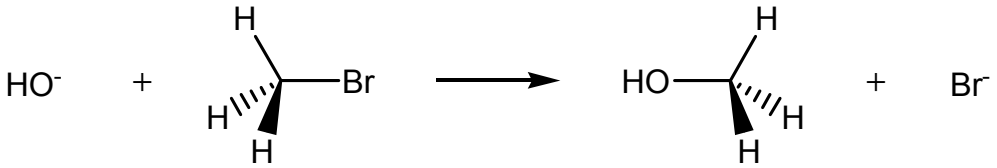
Variation in ΔG^{o} shows up in $\Delta G^{\ddagger}$.

However, this isn't mathematical.

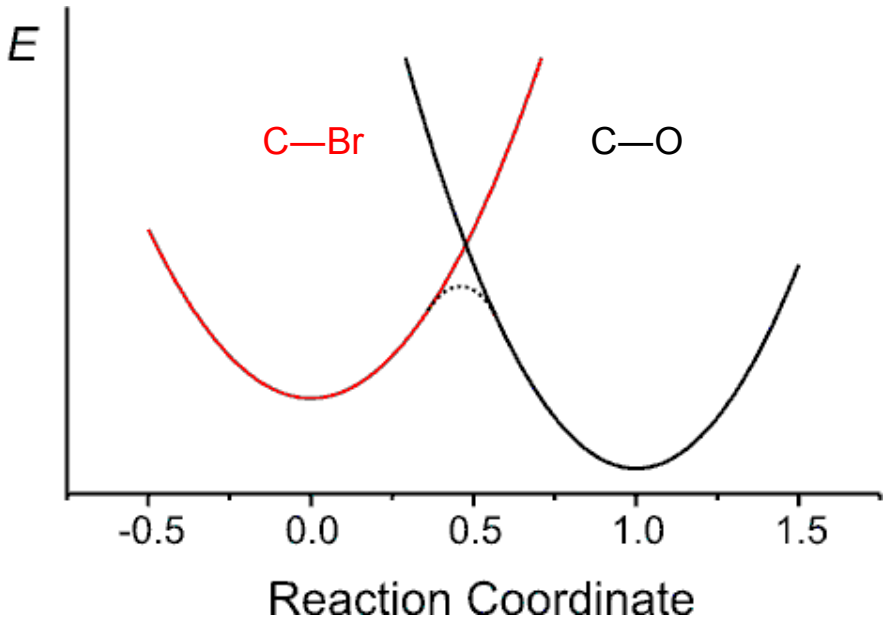
- Can relationship between $\Delta G^{\ddagger}$ and ΔG^{0} be stated mathematically?
- Is Hammond's Postulate correct?

Kinetic-Thermodynamic Connections: Marcus Theory

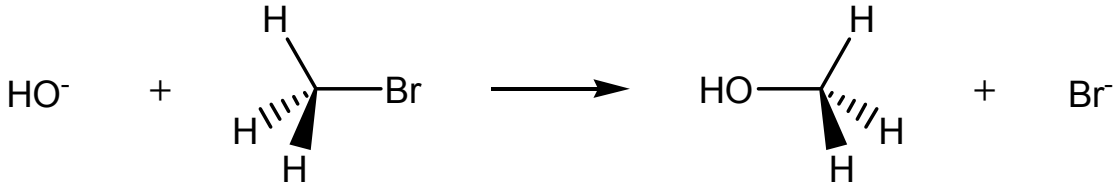
Rudy Marcus (Nobel Prize, 1992):
Reaction coordinate energies can be depicted by simple, intersecting parabolae.



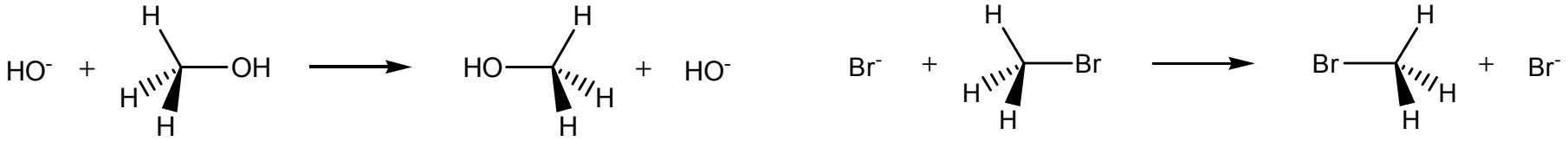
Idea: Use parabola as simple model of bond making and breaking.

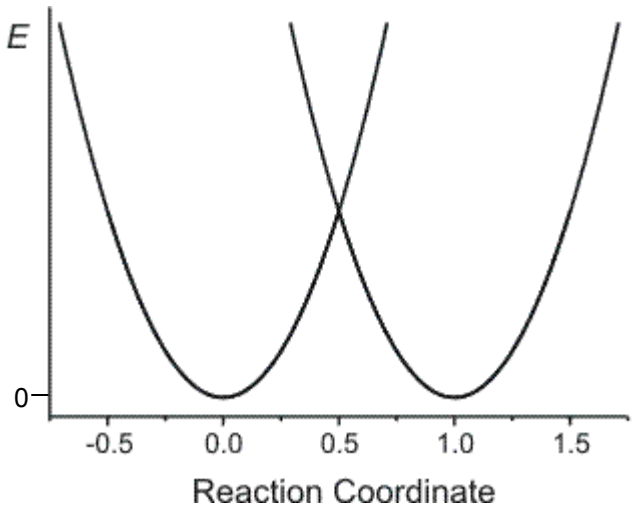


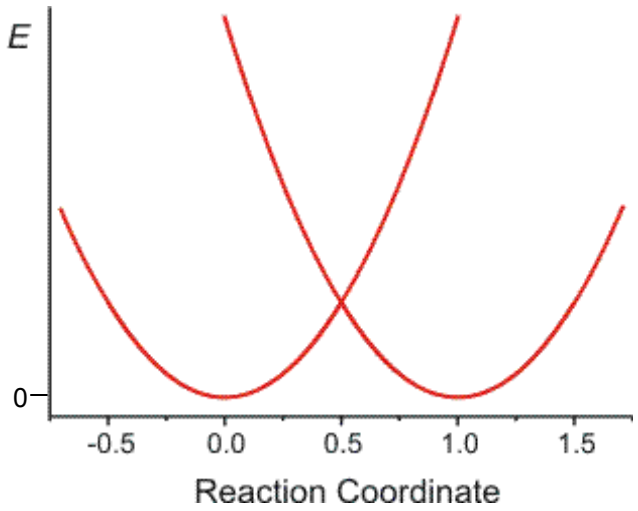
Marcus Theory



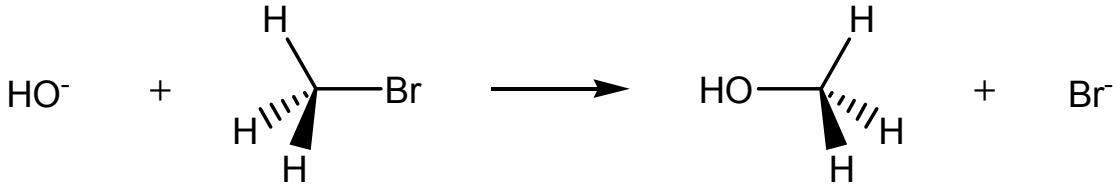
First, consider this reaction to be an amalgamation of two symmetric reactions:







Marcus Theory



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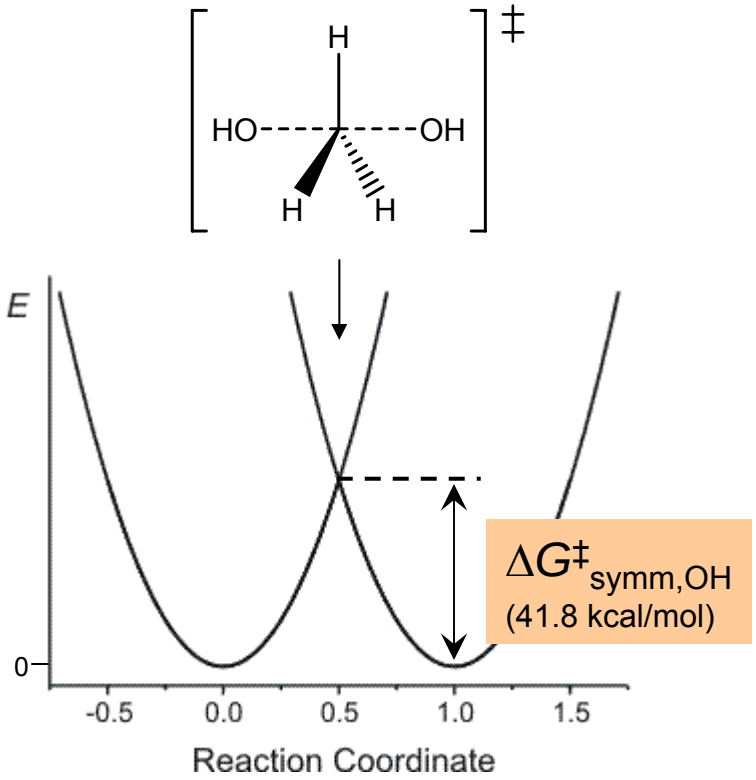
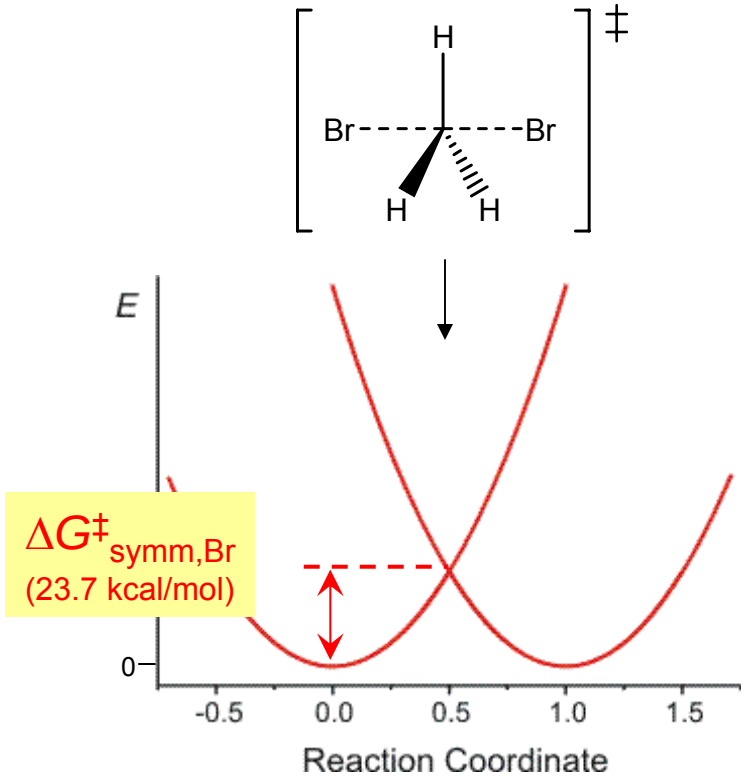
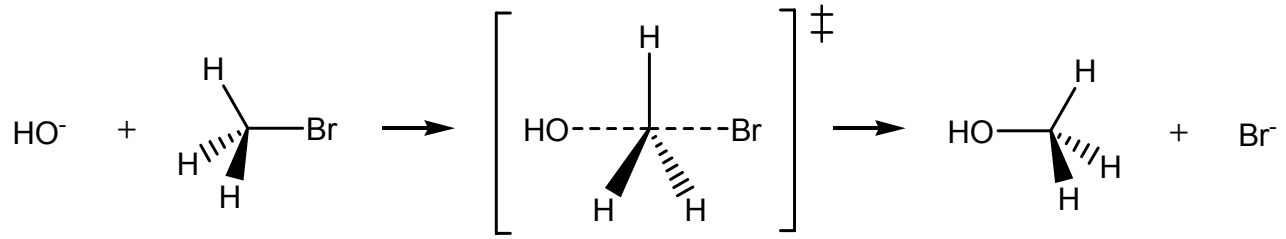
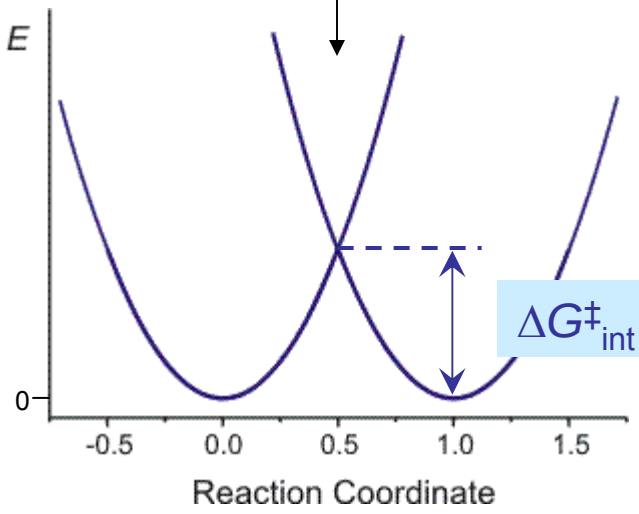




Marcus Theory

Simplify by averaging two potential wells:





$\Delta G^{\ddagger}_{int} = \frac{1}{2}(\Delta G^{\ddagger}_{symm,OH} + \Delta G^{\ddagger}_{symm,Br})$

Marcus Theory

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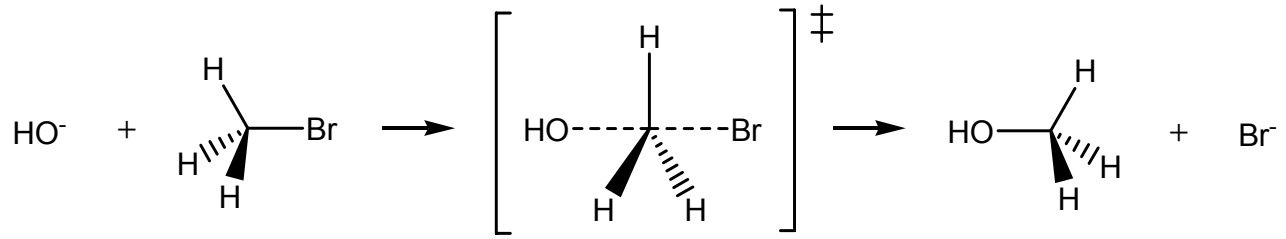
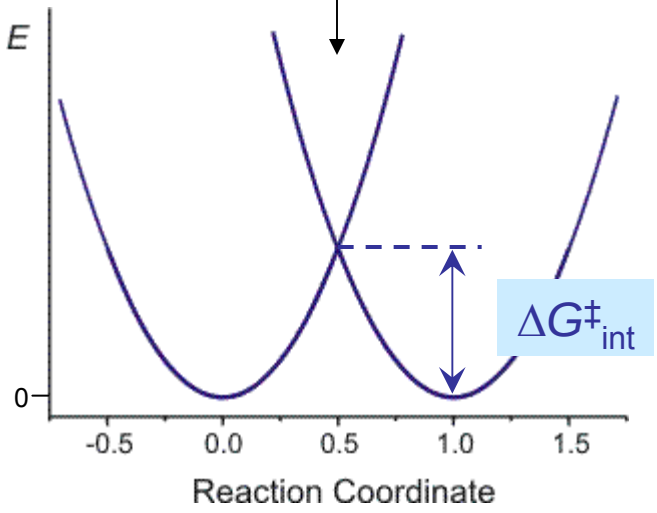
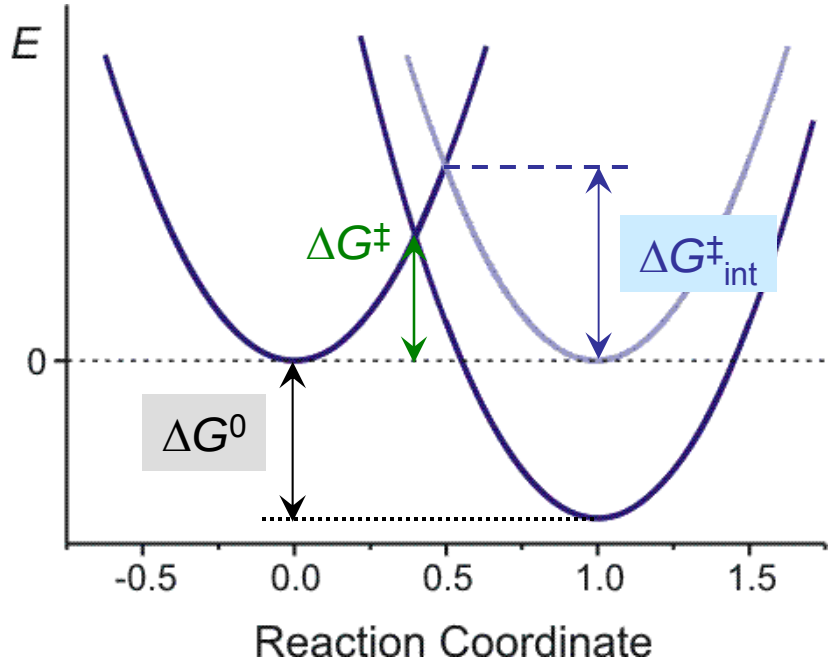




Then, two curves are

$y = 4\Delta G^{\ddagger}_{int} x^2$ and
$y = 4\Delta G^{\ddagger}_{int} (1-x)^2$

But this still isn't right—doesn't include ΔG^0 for the reaction.

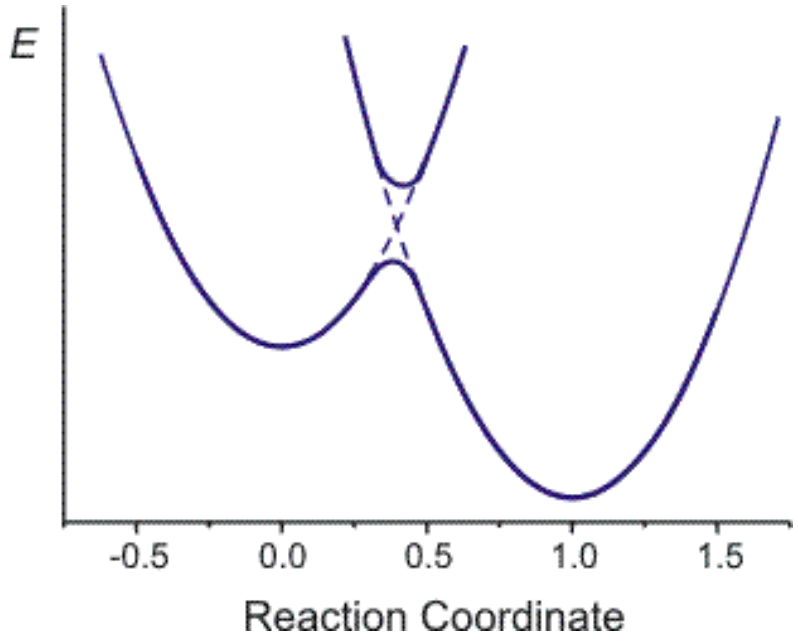


Address exo-/endothermicity by moving right-hand curve.

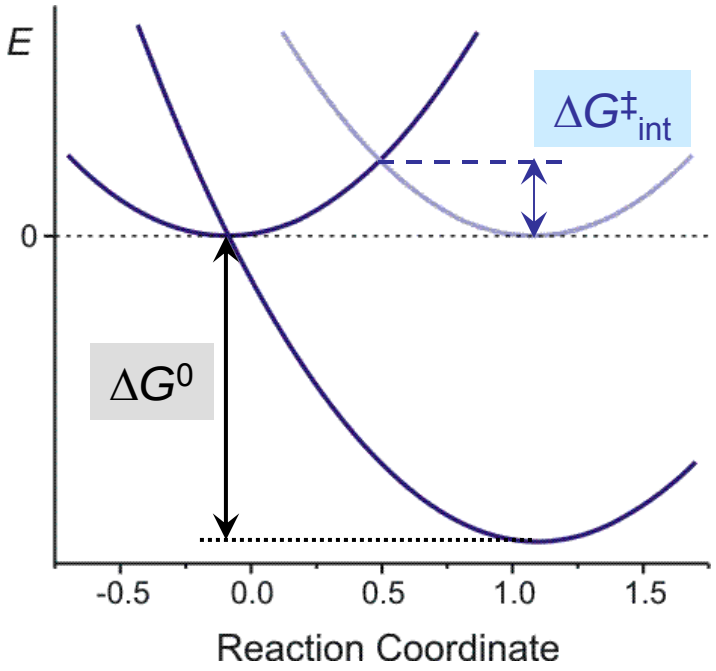
New equations:

$y = 4\Delta G^{\ddagger}_{int} x^2$

$y = 4\Delta G^{\ddagger}_{int}(1-x)^2 + \Delta G^0$

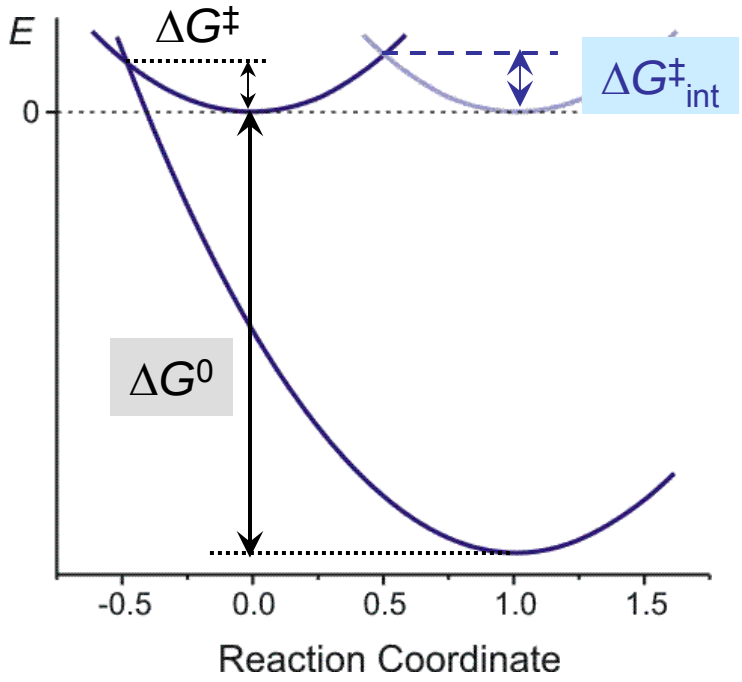


Potential energy surface is actually continuous; contains “avoided curve crossing”



Weird thing at $\Delta G^0 = -4\Delta G^{\ddagger}_{int}$:

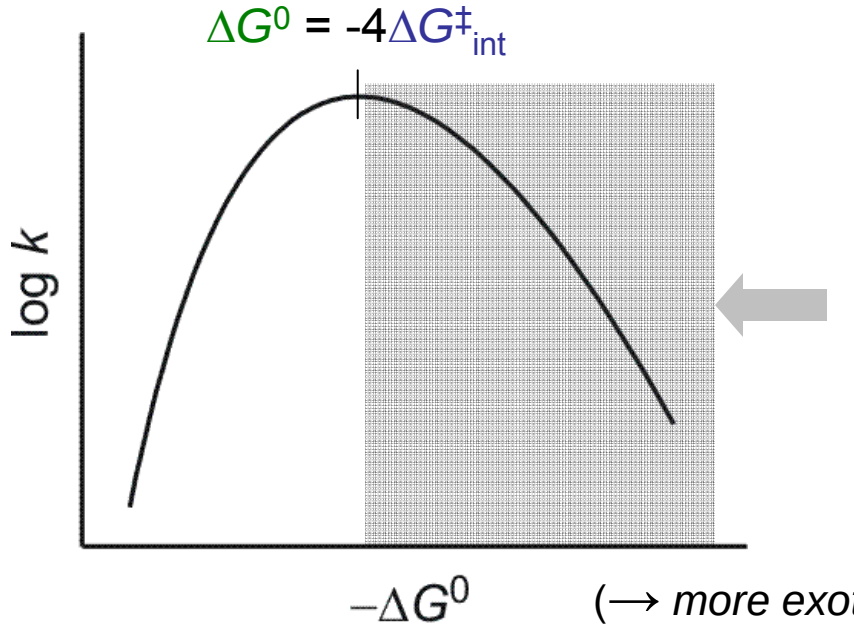
$\Delta G^{\ddagger}$ becomes zero!



Weirder thing at $\Delta G^0 < -4\Delta G^{\ddagger}_{int}$:

$\Delta G^{\ddagger}$ becomes positive again!

Reaction has to backwards to go forwards!



Predicted result:
The "**Marcus Inverted Region**".

Here, *k* decreases with increasing exothermicity.

The Marcus Inverted Region

Very difficult to find reactions fast enough to test this hypothesis.

Need:
- Large thermodynamic driving force
- Low intrinsic barriers

Photoexcitation-Electron transfer:

$$(Ru^{II}L_3^{2+})^* + Fe^{III}L'^{(+)} \longrightarrow Ru^{III}L_3^{3+} + Fe^{II}L'$$

excited-state ion

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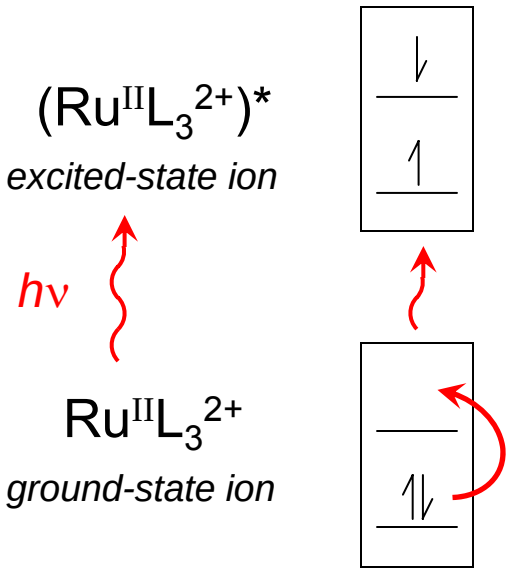

excited electron makes this species a powerful reductant.

Example: Turro, C.; Zaleski, J. M.; Karabatsos, Y. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 6060-6067.

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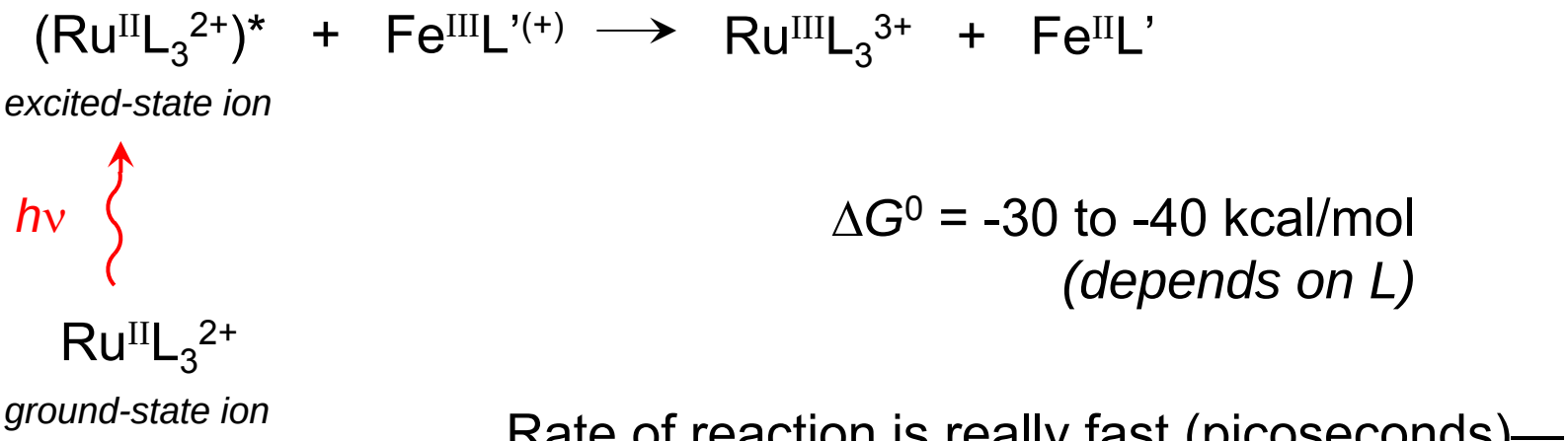


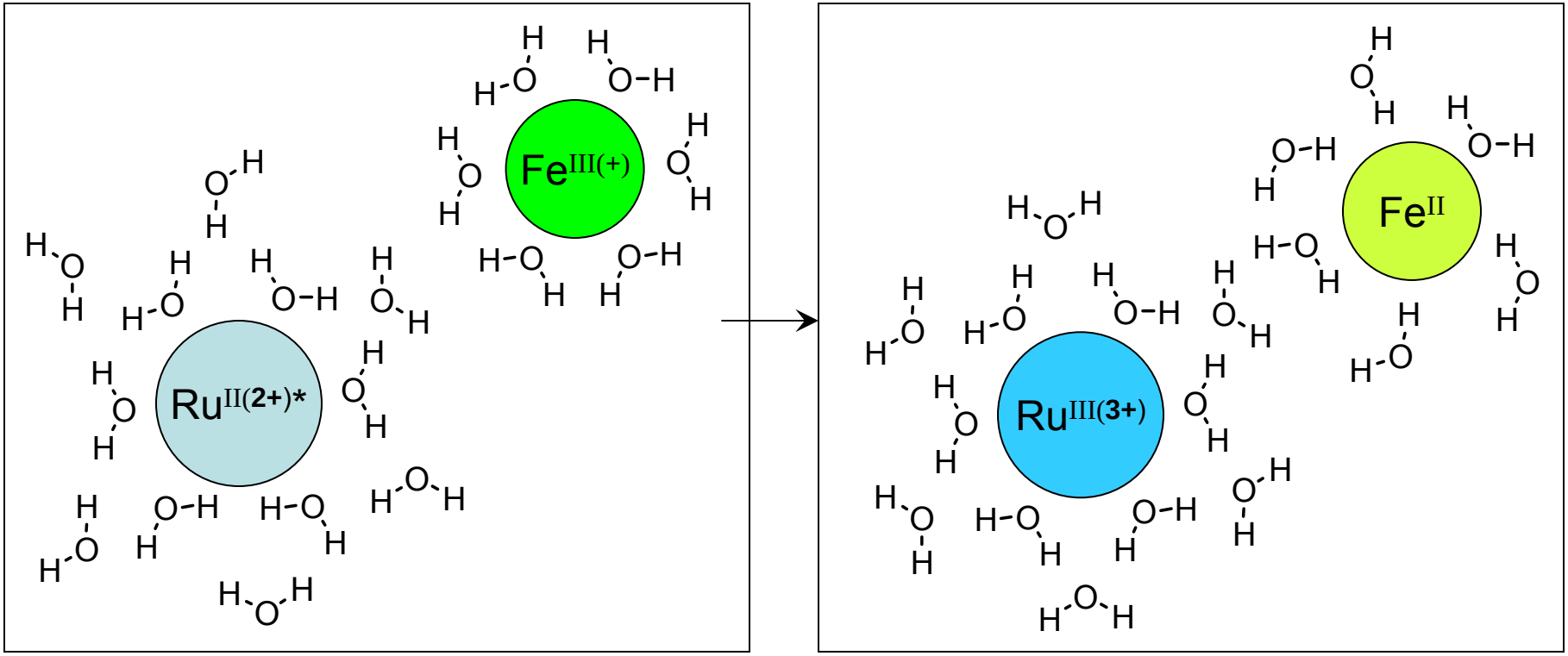
ΔG^0 = -30 to -40 kcal/mol
(depends on L)

Rate of reaction is really fast (picoseconds)—low barrier to electron transfer.

The Marcus Inverted Region

$$(Ru^{II}L_3^{2+})^* \quad + \quad Fe^{III}L'^{(+)} \longrightarrow \quad Ru^{III}L_3^{3+} \quad + \quad Fe^{II}L'$$

In fact, barrier is actually the result of solvent reorganization (rather than electron transfer).



partly ordered partly ordered more ordered less ordered

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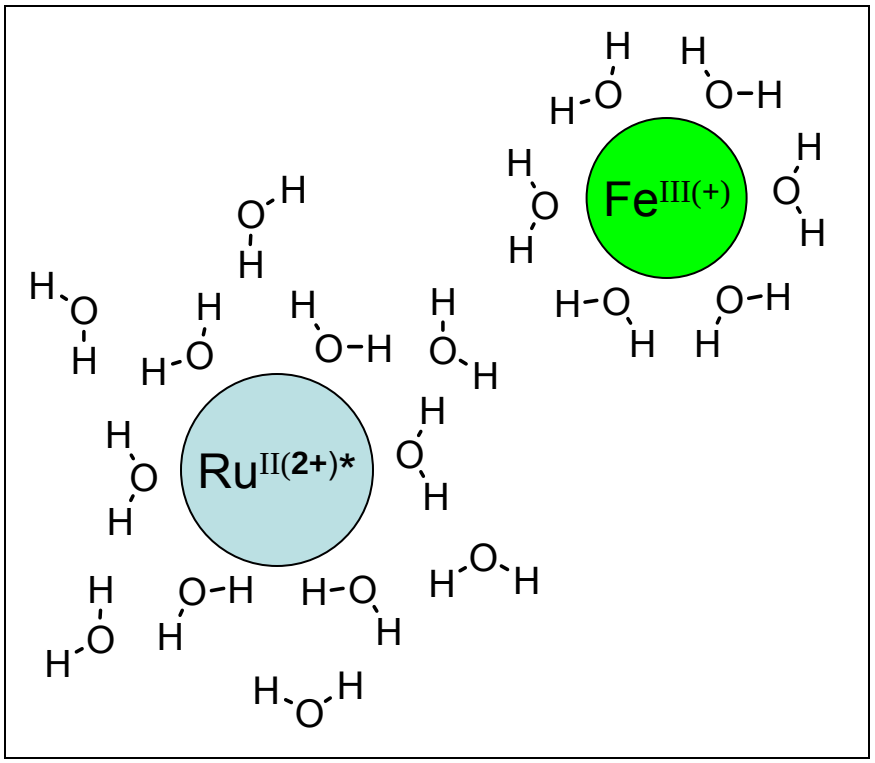

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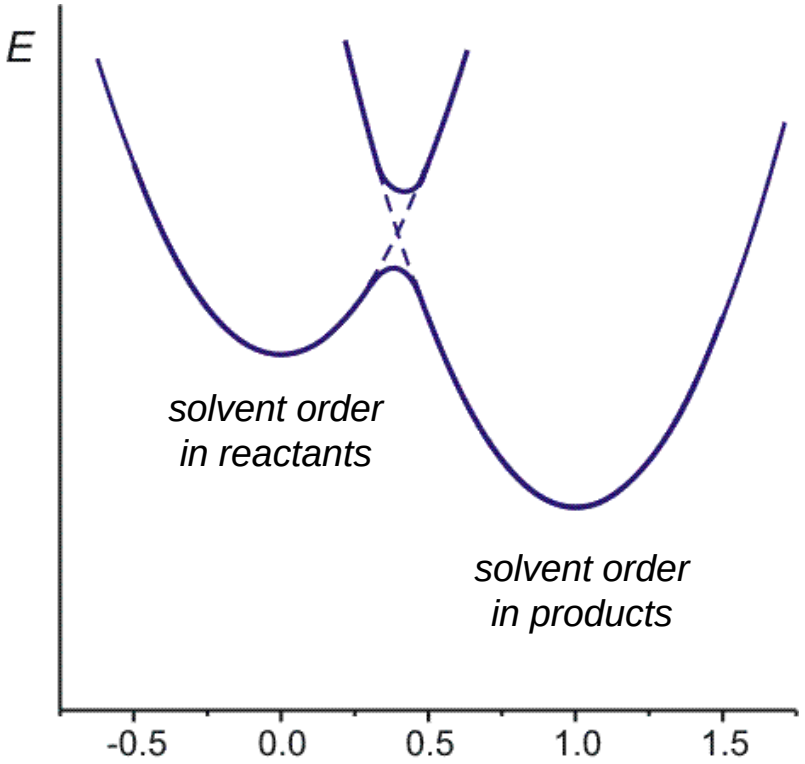

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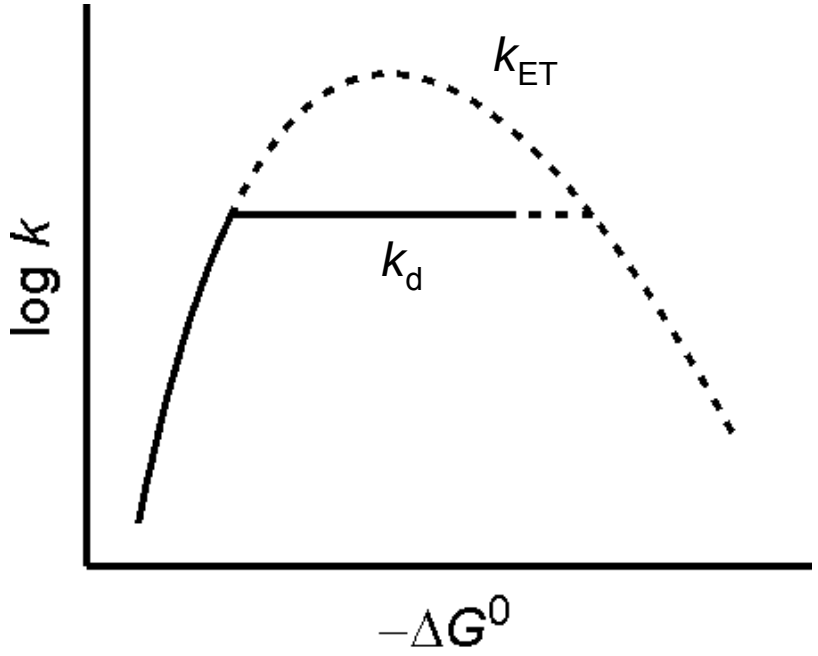
Problem: Reaction is fast, but not faster than diffusion of reactants towards each other;

Rate of reaction limited by rate of diffusion.

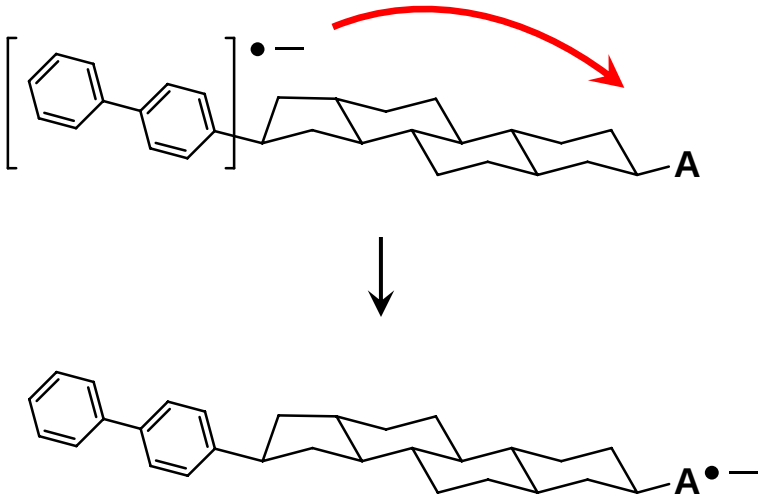


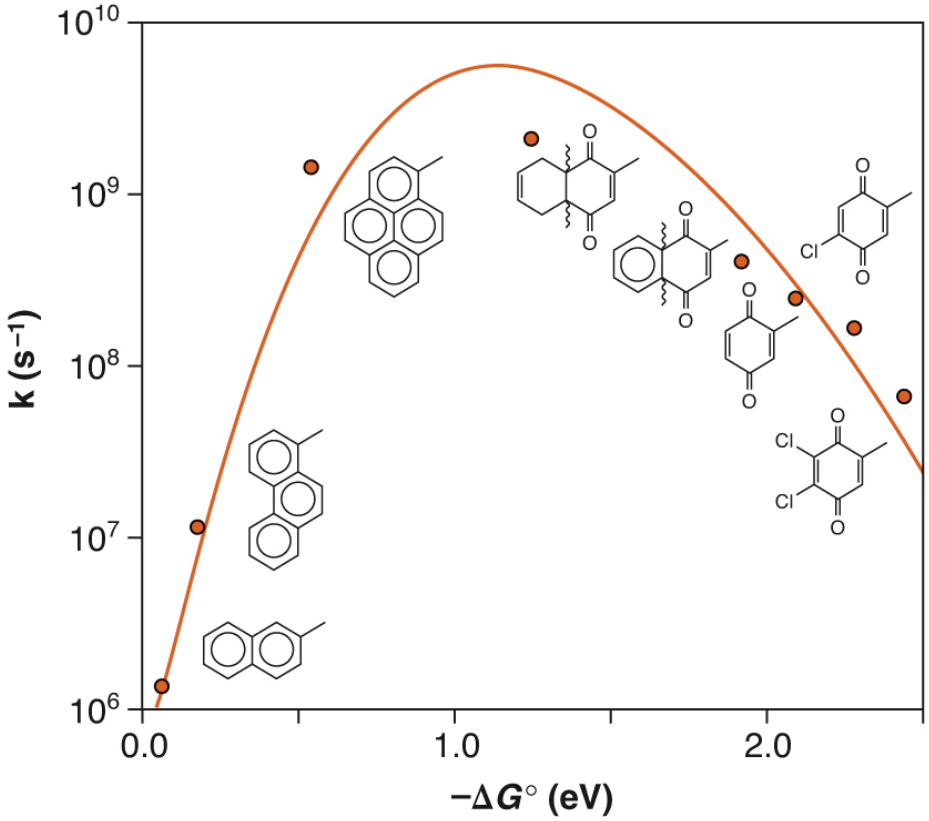
Actual expression:

$$k_{obs} = \frac{k_{ET} k_d}{(k_{ET} + k_d)}$$

The Marcus Inverted Region

Solution: Eliminate diffusion term by attaching reductant to oxidant.

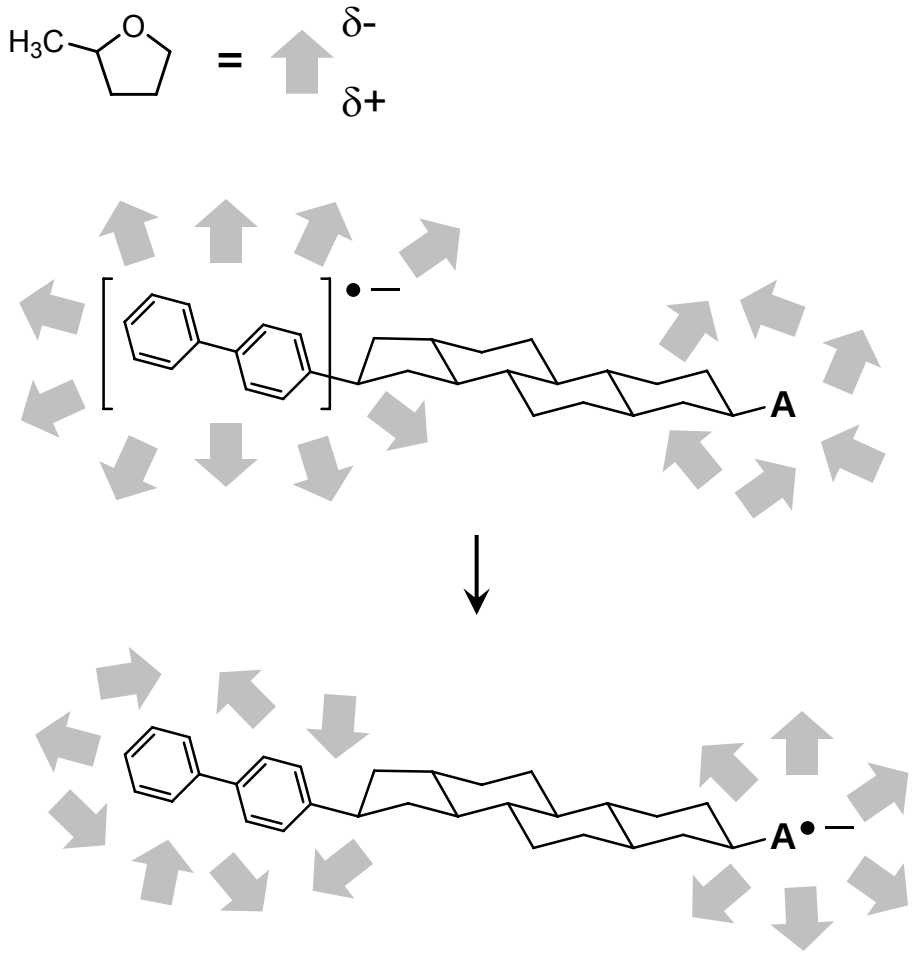


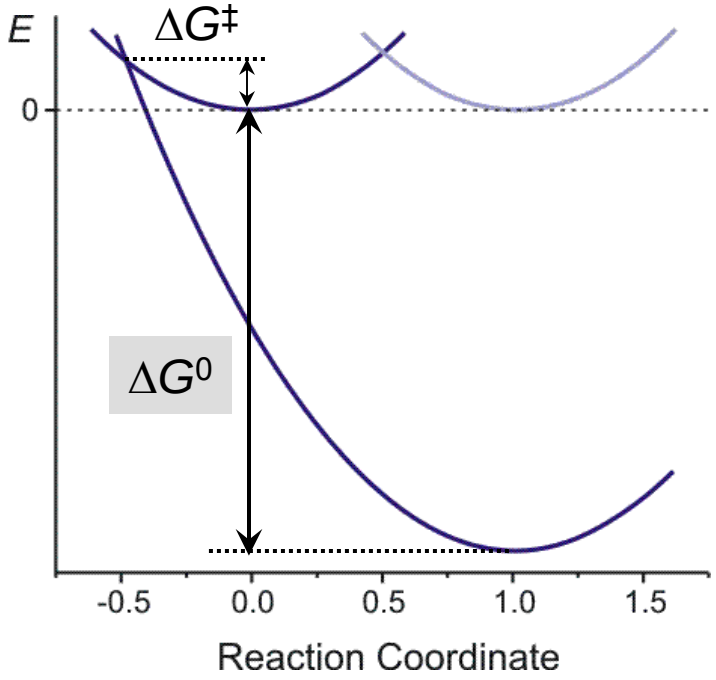


Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

The Marcus Inverted Region

Again, reaction barrier is due to solvent reorganization.





Nonintuitively, solvent has to order more before disordering.