Electron Transfer Theory + Mechanism

① Outer Sphere ET

② Inner Sphere ET

Outer Sphere ET - Redox reaction in which bonds are neither made nor broken

$$[Fe^{II}(CN)_6]^{4-} + [Mo^{III}(CN)_8]^{3-} \xrightarrow{k_{ET} \sim 10^8} [Fe^{III}(CN)_6]^{3-} + [Mo^{IV}(CN)_8]^{4-}$$

This rate is <u>much</u> faster than the rate of ligand exchange ∴ must be outer sphere

outer Sphere ET have 4 fundamental Steps

① $O + R \xrightarrow{k_{diff}} [O \cdots R]$ formation of a precursor complex

② $[O \cdots R] \longrightarrow [O \cdots R]^*$ Activation / Reorganization

③ $[O \cdots R]^* \longrightarrow [\dot{O}^- \cdots R^{\cdot+}]$ ET

④ $[\dot{O}^- \cdots R^{\cdot+}] \longrightarrow O^- + R^{\cdot+}$ dissociation

Importance of activation step is evident from a self exchange Rxn.

Isotopes of Fe + Fe^*

$$[Fe^{III}(OH_2)_6]^{3+} + [{}^*Fe^{II}(OH_2)_6]^{2+} \longrightarrow [Fe^{II}(OH_2)_6]^{2+} + [{}^*Fe^{III}(OH_2)_6]^{3+}$$

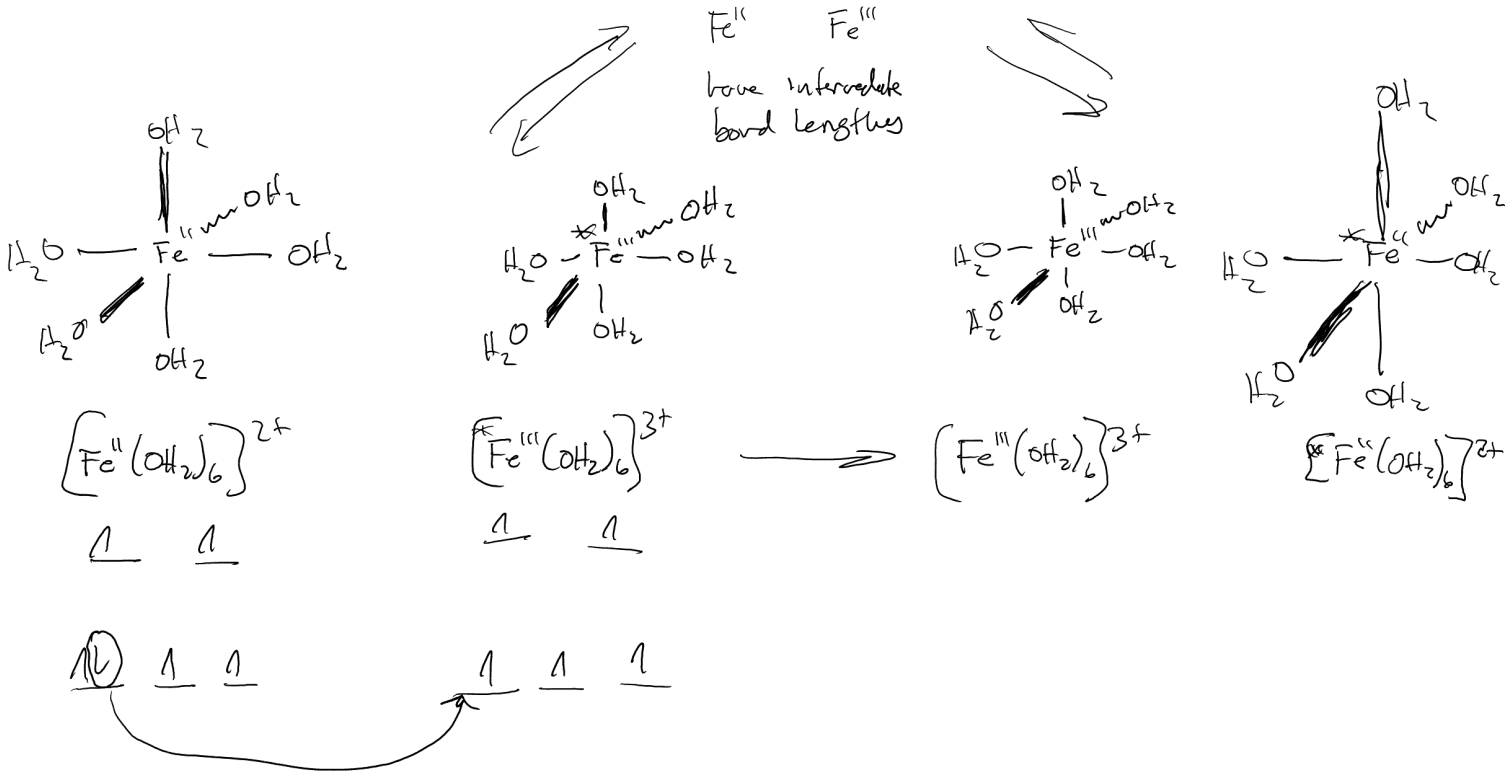
$\Delta G^\ddagger \sim 33\ kJ/mol$ $\quad \Delta G^\ddagger = \Delta G^\ddagger_+ + \Delta G^\ddagger_i + \Delta G^\ddagger_o$

① Reactants must be brought within proper distance for ET

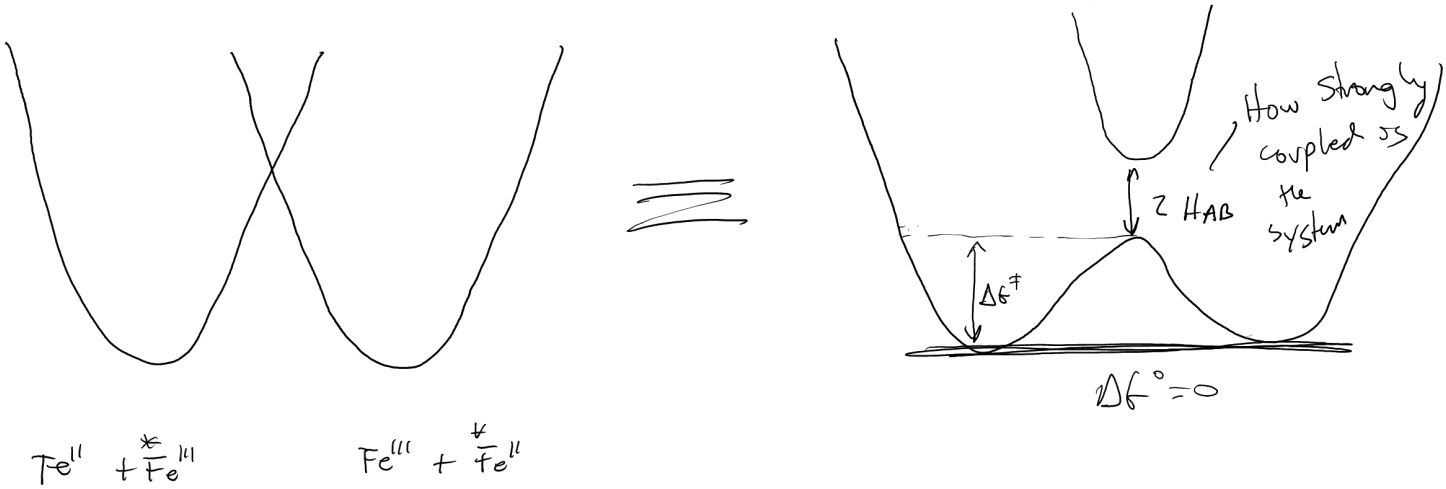
$\Delta G^\ddagger_+$ $\quad k_{ET} = H_{AB}^{\circ}\, e^{-\beta(r_{DA} - r_o)}$

- H_{AB}°: Nature of Ψ
- β: how the medium bet promoting ET
- r_{DA}: center to center distance at contact

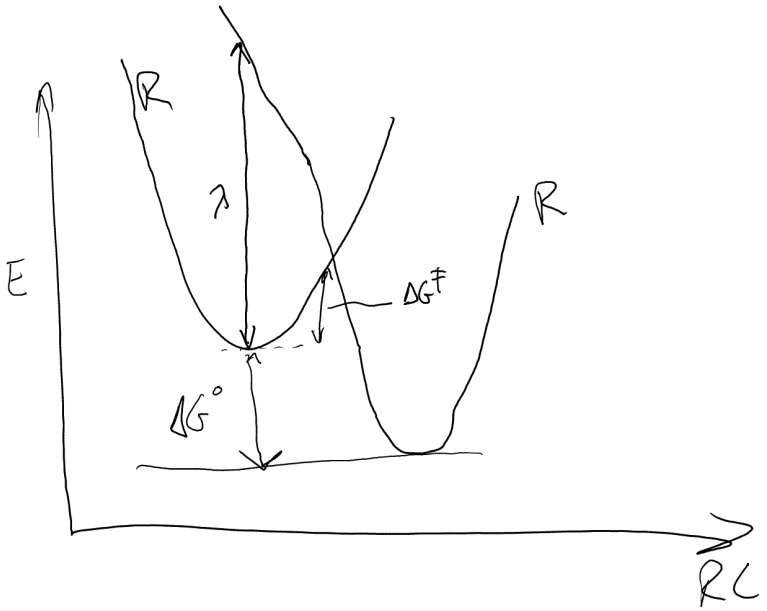
② $\Delta G^{\ddagger}_i$ (Inner Sphere Reorganization Energy)



③ $\Delta G^{\ddagger}_o$ - Outer Sphere Reorganization of the Solvent



$$[Fe^{II}(CN)_6]^{4-} + [M_o^{III}(CN)_8]^{4-} \xrightarrow{\Delta G^\circ < 0} [Fe^{III}(CN)_6]^{3-} + [M_o^{II}(CN)_8]^{3-}$$



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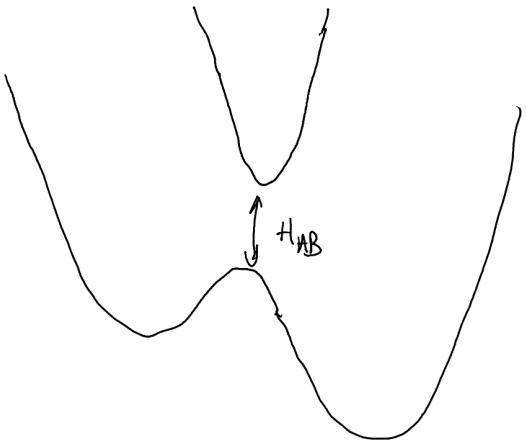


Arhenius Kinetics $\boxed{k_{ET} = A e^{-\Delta G^{\ddagger}/RT}}$

Rudy Marcus - Caltech

J. Chem. Phys. 1956, 24, 944

λ = Reorganization Energy

$$k_{ET} = \underbrace{\frac{2\pi}{\hbar} |H_{AB}|^2 \left(\frac{1}{\sqrt{4\pi\lambda k_b T}}\right) e^{\frac{-(\lambda+\Delta G^\circ)^2}{4\lambda k_b T}}}_{\text{Marcus Theory of ET}}$$

Marcus Theory is critical

① Photosynthesis
② Corrosion
③ Electrocatalysis
④ ETC...

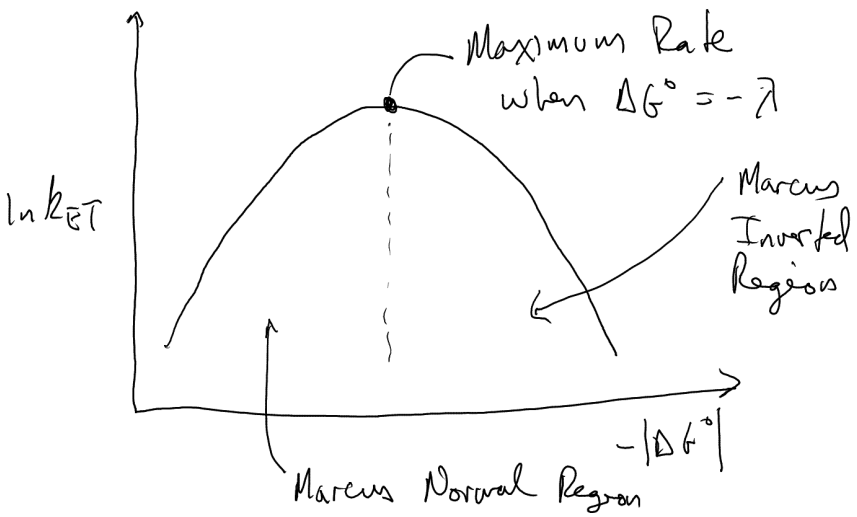
Marcus theory offers a twist on our conceptual thinking about kinetics

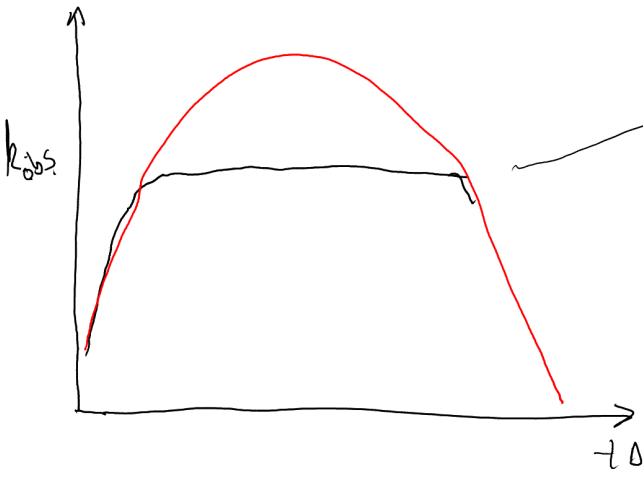
~ In general w/ only worry about $\Delta G^{\ddagger}$ but Marcus tells us that ΔG° + λ are actually important.

If $k_{ET} = A e^{\frac{-(\lambda+\Delta G^\circ)^2}{4\lambda k_b T}}$ $\therefore$ $\ln k_{ET} \propto -(\lambda + \Delta G^\circ)^2$

always positive

This is negative except for when $\Delta G^\circ = -\lambda$





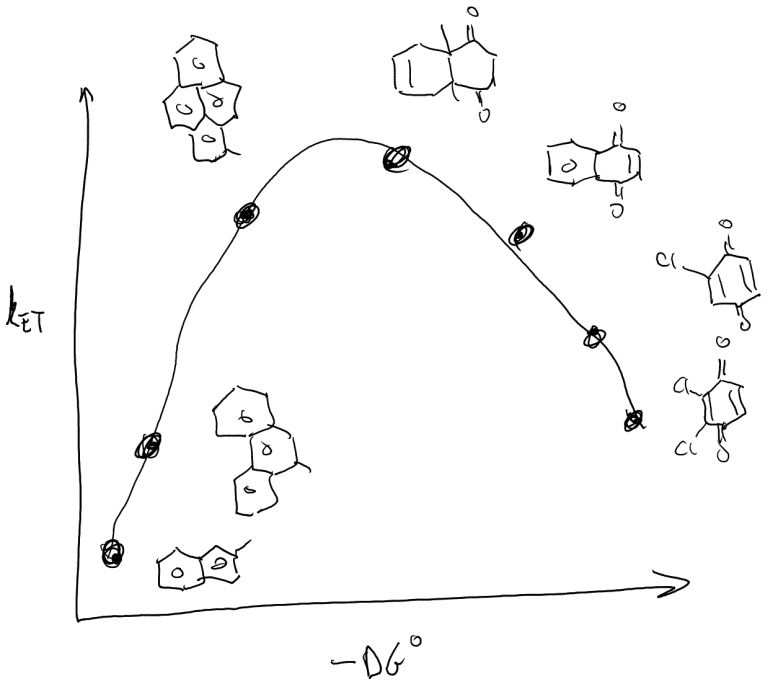
Diffusion Limit $\sim 10^9$
Masks ET Kinetics faster than that...

Bimolecular ET

$D + A \rightarrow D^{\cdot+} + A^{\cdot-}$

$k_{obs} = k_{ET} + k_{diff} = \frac{k_{ET} k_{diff}}{k_{ET} + k_{diff}}$

If 10^{12} If 10^9



In 1986 Closs + Miller prepared a set of Rigid Steroid Linked Donor-Acceptor Dyads

J. Phys. Chem. 1986, 90, 3673

e^- Acceptor

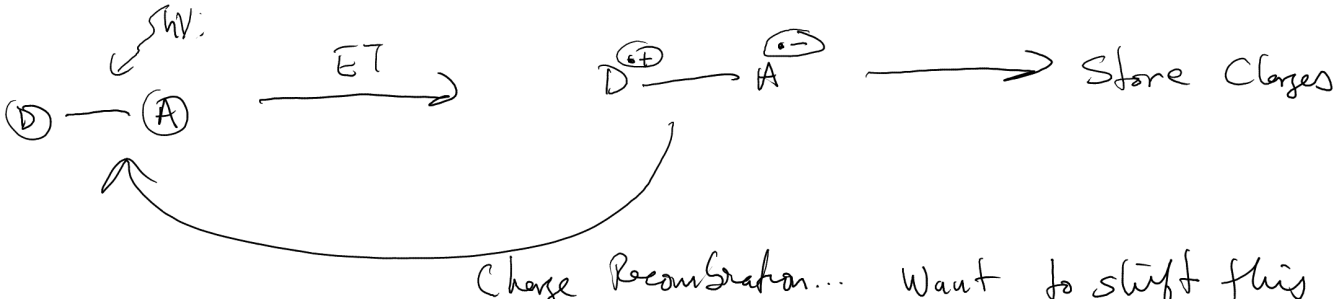
Fairly constant λ overall (A) studied

But $-\Delta G^\circ$ is sensitive to E_{red} potential of various (A)

Harry Gray - Caltech

↳ Marcus Theory important for ET in proteins

Solar Light Capture



Want to shift this to Marcus inverted Region.