Electron Transfer Reactions

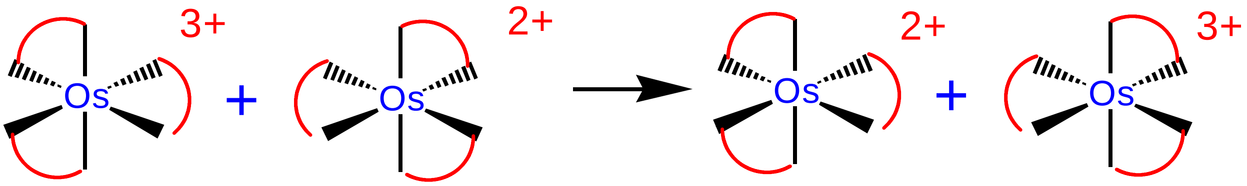
Purcell and Kotz, Ch. 12
Porterfield, Ch. 12:5
S.A.L., p.291-92, 643-49, 807-09

How does permanganate oxidize?

$MnO_4^- + 8H^+ + 5e^-$ 6 $Mn^{2+} + 4H_20$

Answer: question too hard, not on exam, try another one.

1.

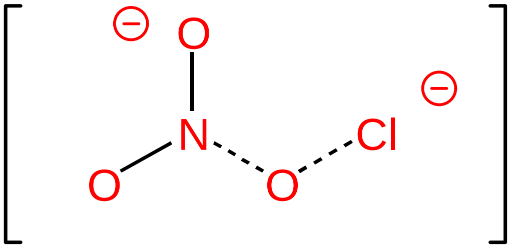


$k = 5x10^4\ M^{-1}s^{-1}$

7) 7)

- ! separately no racemization occurs (what *two* other mechanisms must be considered)
- ! when) Os^{3+} is mixed with 7 Os^{2+}, optical activity is immediately lost.
- ! how does the electron make the jump?
- ! what electron is making the jump?

2.



NO_2^- + OCl^- → NO_3^- + Cl^-

Atom transfer accompanies electron transfer

Redox Reactions at Transition Metal Centers

1. Outer Sphere

No change in coordination sphere of metal
Substitution *INERT* complexes

$$Fe(CN)_6^{4-} \quad + \quad IrCl_6^{2-} \quad \longrightarrow \quad Fe(CN)_6^{3-} \quad + \quad IrCl_6^{3-}$$

Oxid.State	Fe(II)	Ir(IV)	Fe(III)	(Ir(III))
Config’n	(t2g) (eg) (eg)	(t2g) (eg)	(t2g) (eg)	(t2g)
	B F F	B F	B F	B

! what kind of transfer is most difficult/easiest (in terms of structural change)?

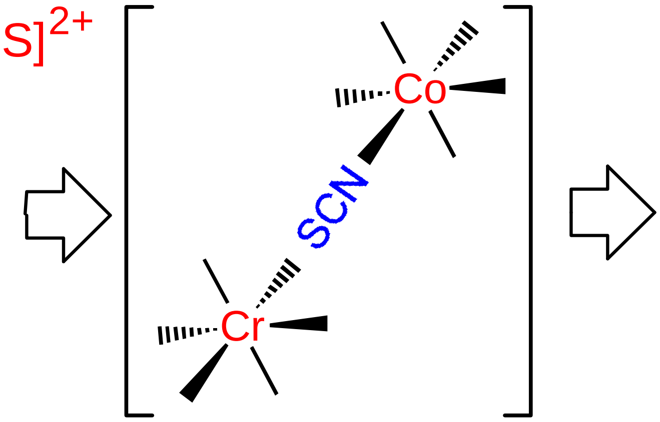
2. Inner Sphere

Requires ligand capable of binding to TWO metal complexes
One metal (reductant) must be *LABILE*

$[Co(NH_3)_5NCS]^{2+}$
config'n =

+

$[Cr(OH_2)_6]^{2+}$
config'n =



$[Co(OH_2)_6]^{2+}$
config'n =

+

$[Cr(OH_2)_5SCN]^{2+}$
config'n =

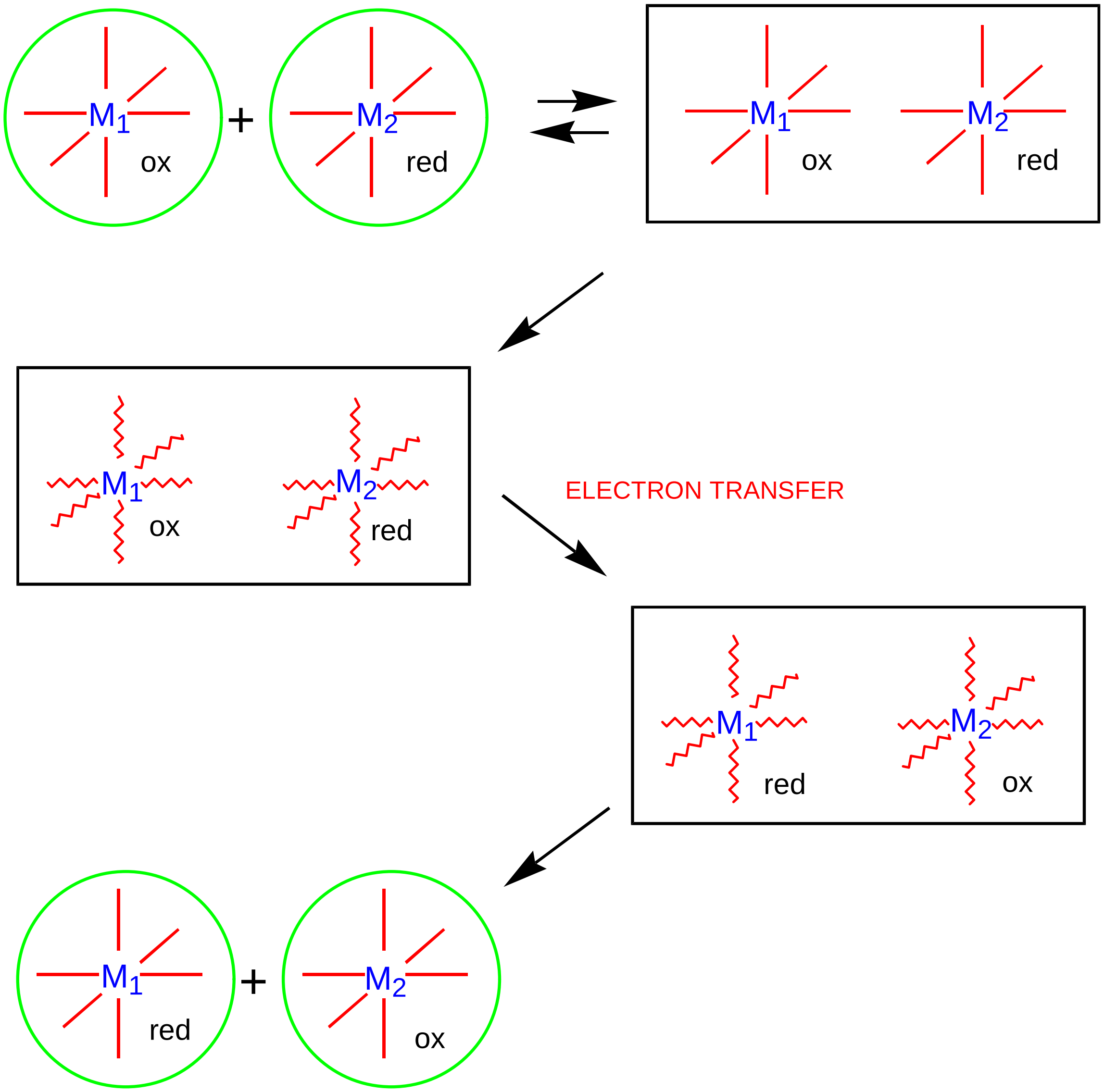
How could you tell the two mechanisms apart?

The Outer Sphere Mechanism

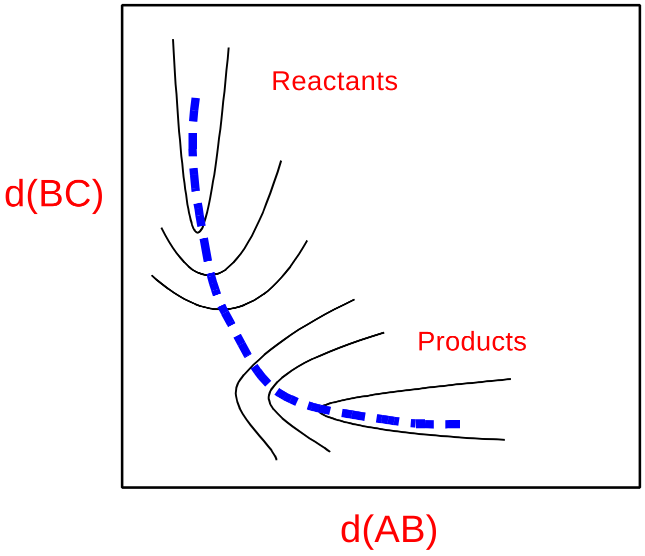
! Formation of a *Precursor Complex* (rapid equilibrium) - involves reorganization of solvent sphere.

! (a) Structural and electronic reorganization to correct configuration.
(b) Electron transfer.
(c) Relaxation to *Successor Complex*.

! Dissociation to separated products.



Parabolas, Wells and Hypersurfaces

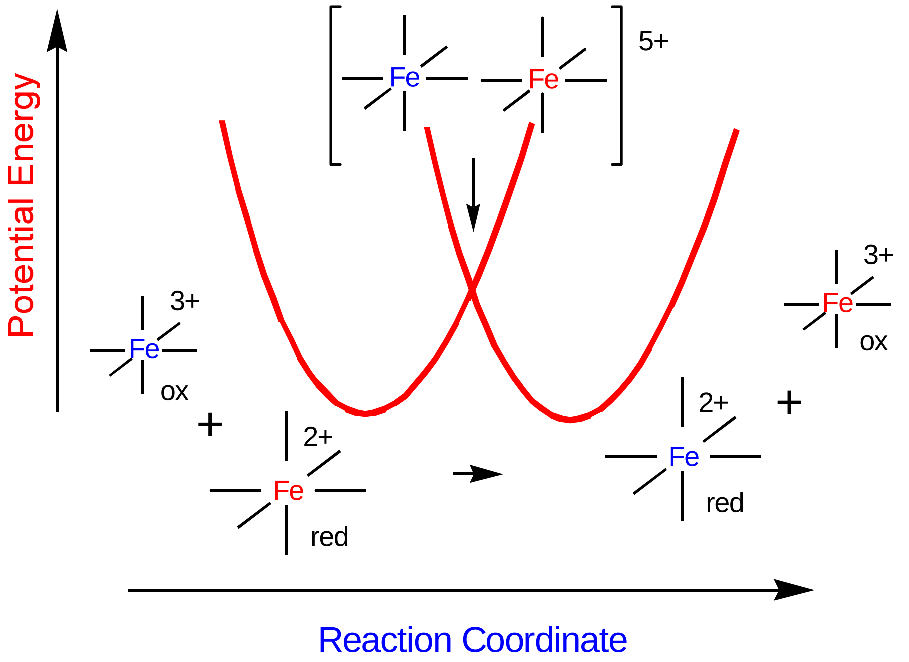


Consider the potential energy changes during a simple substitution reaction,*e.g.*,

AB + C 6 A + BC

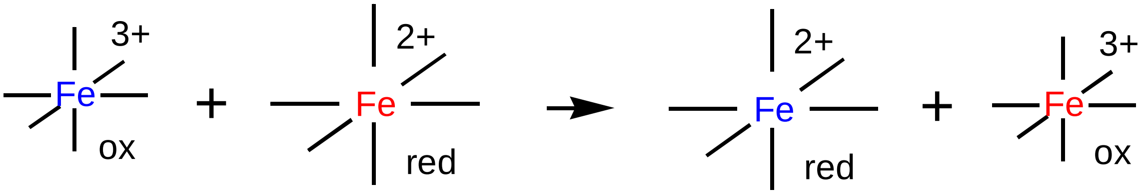
One can draw a simplified COUNTOUR MAP of the *potential energy hypersurface*

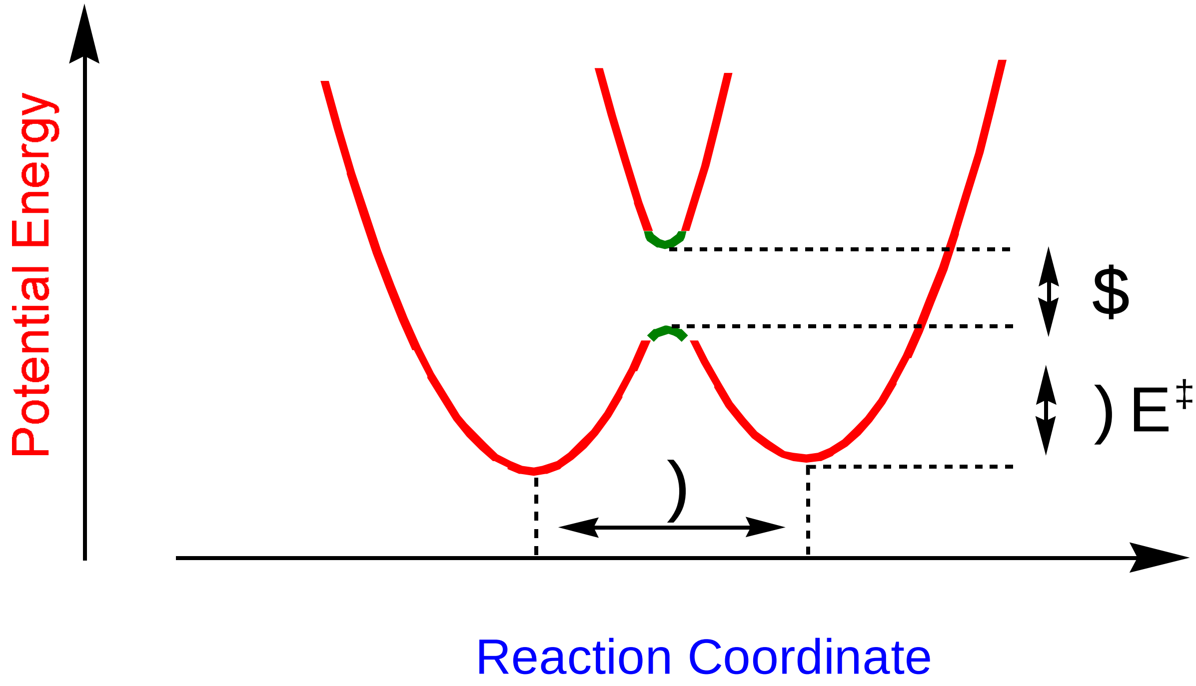
In an outer sphere electron exchange reaction, *no bonds are broken*. A reaction energy profile can built based on two intersecting parabolic energy surfaces. The parabolas symbolize a combined “Harmonic oscillator” or Morse curve for *ALL* the bonds in both reacting molecules.



1. What are the configurations of the reactants/products?
2. Why do bond lengths change?
3. What electron gets transferred?

Structural Activation and Electron Transfer





Activation for electron transfer) $E^{\ddagger}$depends on:

! Extent of structural reorganization) that preceeds electron transfer)

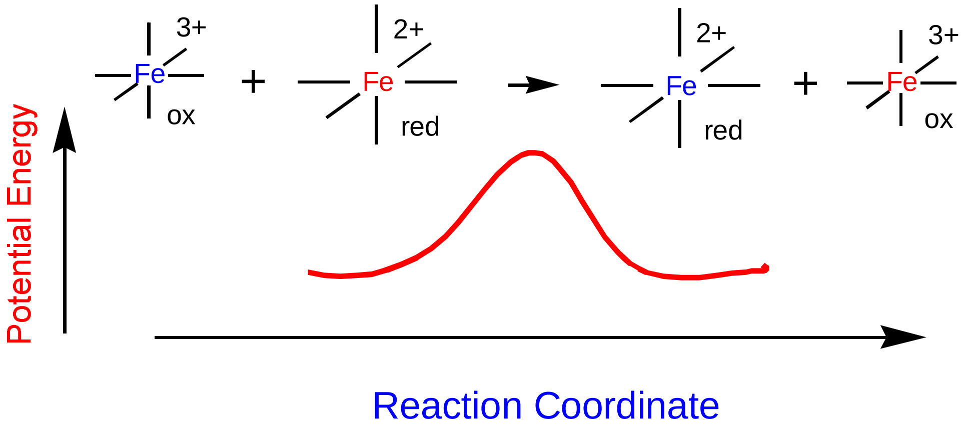
! Ideal ("adiabatic" behaviour, $ = 1) is required, *i.e.*, every time an electron reaches the "window", it must be able to get through

Whatever ground state configurations are involved, structures must "shuffle around" until a B to B transfer is possible.

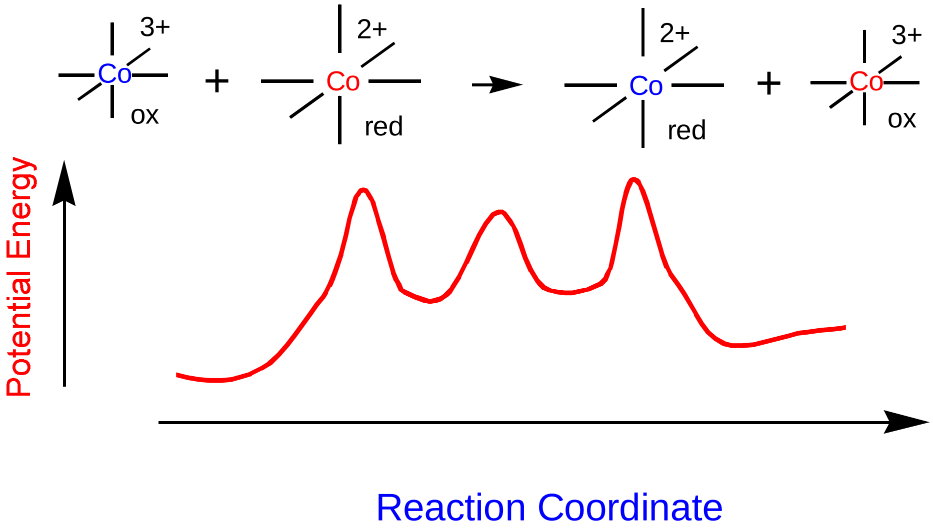
Most fast outer sphere reactions are found with large flat organic ligands (*e.g.*, bipy) which facilitate B to B transfer.

Electronic Reorganizations for Outer Sphere Transfers

Case 1. Fe(II) (high spin) to Fe(III) (high spin) exchange



Case 2. Co(II) (high spin) to Co(III) (low spin) exchange



In each case what are the ground state configurations, and what configurational changes are necessary to ensure a B to B transfer?

Rationalize the rates of the following Outer Sphere Reactions

Reaction				Rate ($M^{-1}s^{-1}$)
$Fe(H_2O)_6^{2+}$ B^4F^2	+	$Fe(H_2O)_6^{3+}$ B^3F^2	(*net* B to B) 6	4.0
$Fe(phen)_3^{2+}$ B^6	+	$Fe(phen)_3^{3+}$ B^5	(*net* B to B) 6	3×10^7
$Ru(phen)_3^{2+}$ B^6	+	$Ru(phen)_3^{3+}$ B^5	(*net* B to B) 6	3×10^7
$Co(NH_3)_6^{2+}$ B^5F^2	+	$Co(NH_3)_6^{3+}$ B^6	(*net* F to F) 6	10^{-9}
$Co(phen)_3^{2+}$ B^5F^2	+	$Co(phen)_3^{3+}$ B^6	(*net* F to F) 6	1.1

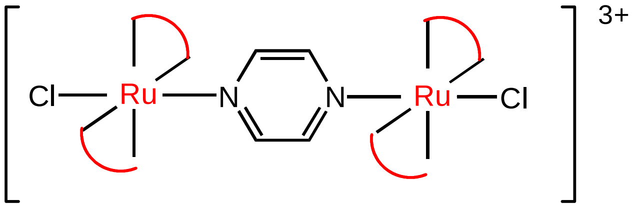
! *Which reactions will involve large changes in d(M-L)?*

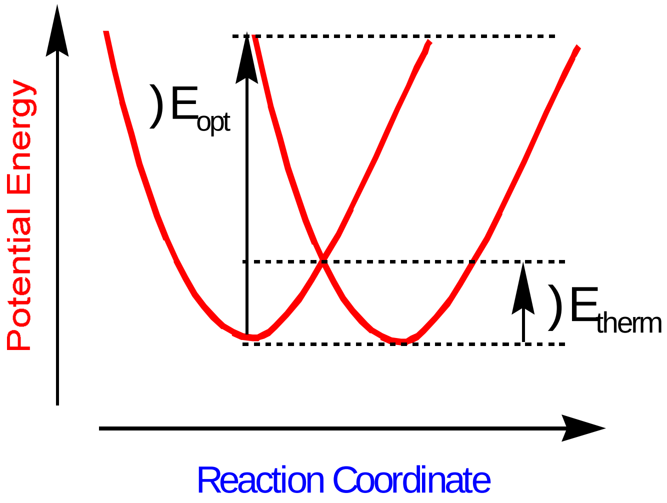
! *What kind of ligands will enhance the rate?*

M	L	d(M(II)-L) in D	d(M(III)-L) in D
Ru	NH_3	2.144	2.104 (small))
Co	NH_3	2.114	1.936 (large))
Fe	bipy	1.97	1.963 (small))
Co	bipy	2.128	1.93 (large))

Optical and Thermal Intervalence Electron Transfer

Many "Mixed Valence" Compounds show a low energy intervalence charge transfer band (often in the near infrared region). Consider Taube's complex:





What are the Ru oxidation states?

Optical transfer occurs "vertically", with no change in structure. Why?

Can you derive a relationship (based on properties of parabolas) for the ratio of $)E_{optical}$ to $)E_{thermal}$?

Exercise: Taube's complex shows an IT band a 7960 cm^{-1}. Estimate a value for the rate of thermal electron transfer between the two ruthenium metal centres.

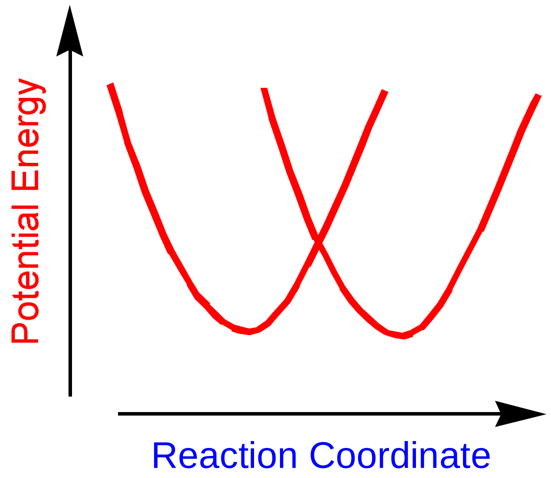
Cross Reactions and /Marcus-Hush Theory

$$M_A^{x+} \quad + \quad M_B^{y+} \quad W \quad M_A^{(x-1)+} \quad + \quad M_B^{(y+1)+}$$

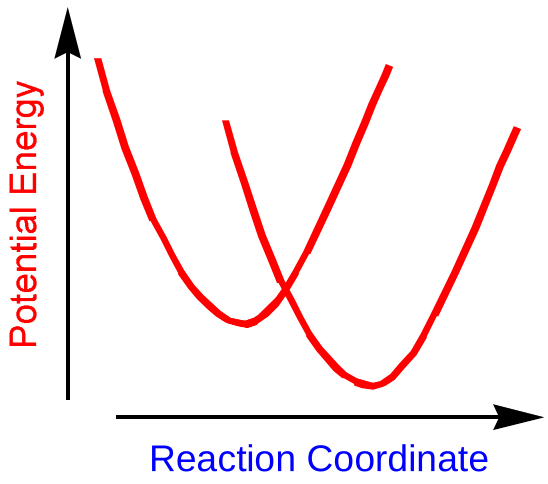
If A = B this is an *exchange reaction*. If A …B this is a *cross reaction.*

Unlike exchange reactions cross reactions are often quite rapid in spite of an otherwise large chemical activation.

An Exchange Reaction



A Cross Reaction



The cross reaction rate constant k_{12} is:

$$k_{12} = [k_1 k_2 K_{12} f]^{1/2}$$

k_1 and k_2 are self exchange rates for M_A and M_B
K_{12} is the equilibrium constant
f is frequency factor (often set = 1 to make life simple)

Likewise:

$$)G_{12}^{\ddagger} = \frac{1}{2}[)G_1^{\ddagger} +)G_2^{\ddagger}] + \frac{1}{2})G_{12}^{0}$$

(See Sutin and Creutz, *J. Chem. Educ.*, **60**, 809 (1983))

Using Marcus theory, rates of cross reactions can be predicted from self exchange rate data and cell potentials.

Reaction	E^0(V)	k_{obs} ($M^{-1}s^{-1}$)	$k_{calc.}$
$V(H_2O)_6^{2+}$ 6 $V(H_2O)_6^{3+}$ + e	0.26	1×10^{-2}	
$Cr(H_2O)_6^{2+}$ 6 $Cr(H_2O)_6^{3+}$ + e	0.41	2×10^{-5}	
$Co(en)_3^{2+}$ 6 $Co(en)_3^{3+}$ + e	0.24	2×10^{-5}	
$Co(phen)_3^{2+}$ 6 $Co(phen)_6^{3+}$ + e	-0.42	5	
$Cr^{2+} + Co(en)_3^{3+}$ 6	0.17	3×10^{-4}	5×10^{-4}
$Cr^{2+} + Co(phen)_3^{3+}$ 6	0.83	3×10^{1}	1×10^{4}
$V^{2+} + Co(en)_3^{3+}$ 6	0.02	7×10^{-4}	6×10^{-4}
$V^{2+} + Co(en)_3^{3+}$ 6	0.68	4×10^{3}	2×10^{4}

Remember that $)G_{12}^0 = - RT \ln K_{12} = - n F E^0$

Inner Sphere Electron Transfer

The outer sphere pathway is “default”. If the rate of electron transfer is significantly greater than Marcus Theory predicts, then an inner sphere pathway must be invoked.

$$[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+} \overset{H^+}{6} [Co(H_2O)_6]^{2+} + [Cr(H_2O)_6]^{2+} + 6NH_4^+$$

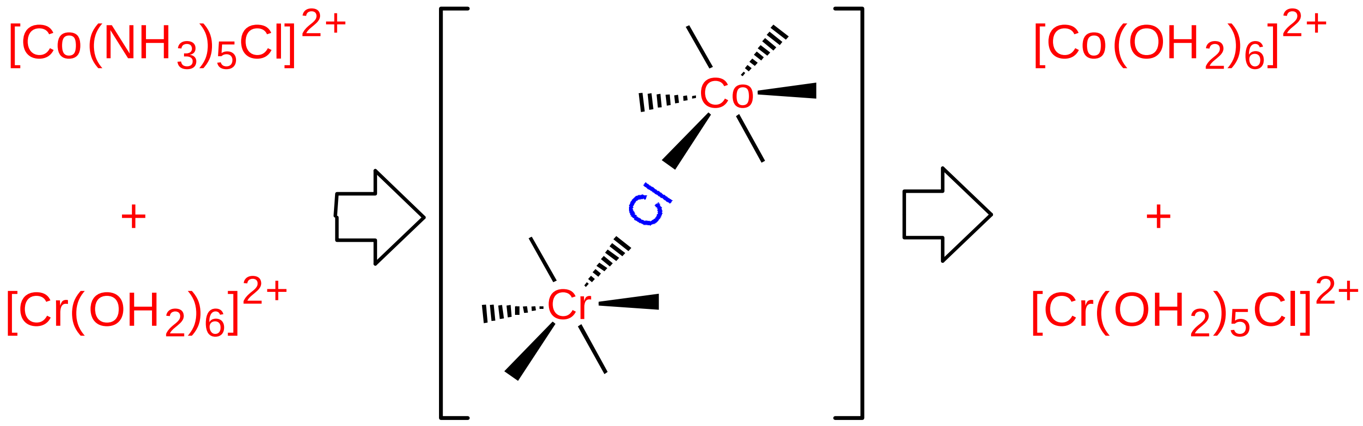
B^6 $B^3\ F^1$ $B^5\ F^2$ B^3

$k = 10^{-3}\ M^{-1}s^{-1}$. A nice, slow (*net* F* 6 F*) outer sphere reaction.

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \overset{H^+}{6} [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_4^+$$

B^6 $B^3\ F^1$ $B^5\ F^2$ B^3

$k = 5 \times 10^5\ M^{-1}\ s^{-1}$. This reaction finds the “*side door*” inner sphere route.



Features required for Inner Sphere Mechanism

! A ligand capable of binding to *TWO* metal complexes, *e.g.*, (Cl^-, NCO^-, OH^-, N_3^-).

! One metal (reductant) must be *LABILE*, in order to generate vacant site for bridge.

Ox-X + Red 6 [Ox--X--Red] 6 Ox$^-$ + Red$^+$
inert *labile* *labile* *inert*

Electron is transferred through the F-system of the bridge (not the B-system), *i.e.*, the electronic set-up must allow for F to F transfer.
We can now understand the following rate enhancements . . .

				(Rate IS)/(Rate OS)
Cr^{2+} B^3 F^1	+	Co^{3+} B^6	6 F* 6 F*	10^{10}
Cr^{2+} B^3 F^1	+	Ru^{3+} B^5	6 F* 6 B	10^2
V^{2+} B^3	+	Co^{3+} B^6	6 B 6 F*	10^2
V^{2+} B^3	+	Ru^{3+} B^5	6 B 6 B	no data, all reactions are OS[†]

[†] Products and reactants are *INERT*, orbital requirements are wrong too. The inner sphere “side door” is *locked*!

Nature of Bridging Ligand

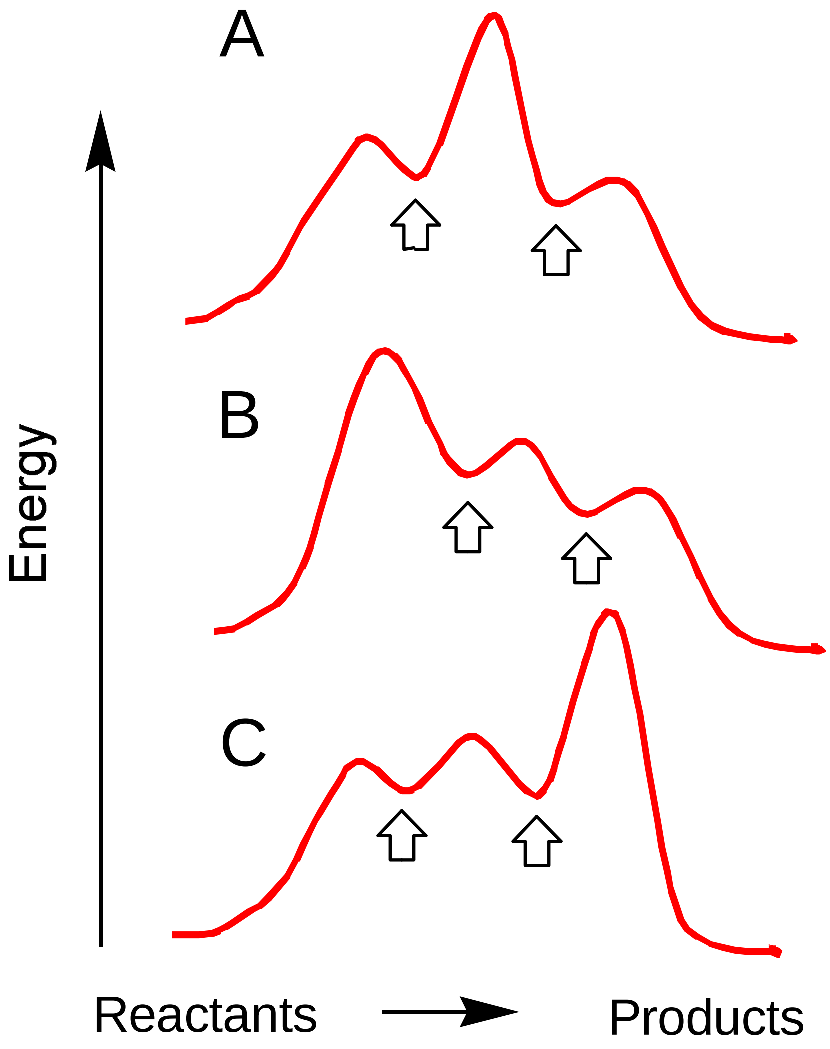
Rate constants for the reduction of $Co(NH_3)_5L^{3+}$ by $Cr(H_2O)_6^{2+}$

L	*k*, $M^{-1}\ s^{-1}$
NH_3	8.0×10^{-5}
F^-	2.5×10^{5}
Cl^-	6.0×10^{5}
Br^-	1.5×10^{6}
I^-	3.0×10^{6}
N_3^-	3.0×10^{6}
OH^-	1.5×10^{6}
H_2O	*ca.* 0.1
(Co)-NCS^-	19
(Co)-SCN^-	2×10^{5}

Factors to consider:

- Size (orbital overlap)
- No. of lone pairs
- Soft and hard “ends”

Summary of Inner Sphere Reaction Profiles



(A) Electron transfer is rate determining (a perfect F* 6 F*)

(B) Bridged precursor formation is rate determining, e.g., reductions by V^{2+} (loss of water is very slow), so slow that reactions are always outer sphere.

(C) Break-up of successor complex is rate determining, *e.g.*,

$Ru(NH_3)Cl^{2+} + Cr(H_2O)_6^{2+}$ 6 $Ru(II) + CrCl^{2+}$

(the tape on the fingers problem)