Redox Reactions: Electron Transfer
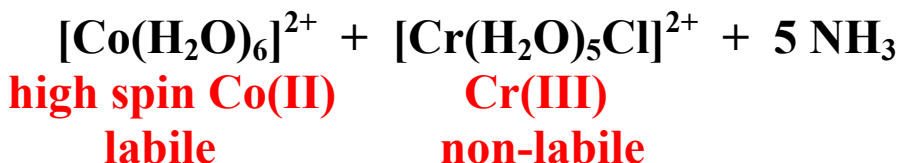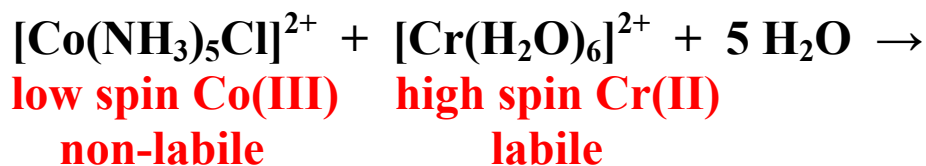
(see H&S, 3rd Ed. Sect. 26.5, pp. 895-900)

Inner Sphere: **bridge bond formed between redox partners and the bridging group often (though not always) transfers**

Outer Sphere: **no direct bond between redox partners and no change in coordination sphere**

Inner sphere mechanism – three distinct steps:

1) substitution to form a bridge between oxidant and reductant
2) actual electron transfer
3) separation of the products (often with transfer of the bridge ligand)

Taube's classical 1953 experiment (Nobel Prize 1983):

$[Co(NH_3)_5Cl]^{2+}$ + $[Cr(H_2O)_6]^{2+}$ + 5 H_2O →
low spin Co(III)   **high spin Cr(II)**
   non-labile   **labile**

$[Co(H_2O)_6]^{2+}$ + $[Cr(H_2O)_5Cl]^{2+}$ + 5 NH_3
high spin Co(II)   **Cr(III)**
     labile   **non-labile**

Proceeds via the following steps:

1) $[Co(NH_3)Cl]^{2+} + [Cr(H_2O)]^{2+} \rightarrow$

$$[(NH_3)_5Co(\mu\text{-}Cl)Cr(H_2O)_5]^{4+} + H_2O$$

2) $[(NH_3)_5Co(\mu\text{-}Cl)Cr(H_2O)_5]^{4+} \rightarrow [(NH_3)_5Co(\mu\text{-}Cl)Cr(H_2O)_5]^{4+}$

Co(III) / Cr(II)   Co(II) / Cr(III)

3) $[(NH_3)_5Co(\mu\text{-}Cl)Cr(H_2O)_5]^{4+} + H_2O \rightarrow$

$$[(NH_3)_5Co(H_2O)]^{2+} + [ClCr(H_2O)_5]^{2+}$$

high spin Co(II)   Cr(III)

labile   non-labile

followed by a 4th step in this case, because the Co(II) product is substitution labile:

4) $[(NH_3)_5Co(H_2O)]^{2+} + 5\,H_2O \rightarrow [Co(H_2O)_6]^{2+} + 5\,NH_3$

How do we know Cl⁻ doesn't fall off before or after electron transfer?

Both the starting Co^{3+} (d^6) and product Cr^{3+} (d^3) chloride complexes are substitutionally inert so Cl⁻ transfer must have occurred via a bridge species.

It is possible for any of the three steps to be rate limiting depending on the particular ligand set and metal d^n count:

Egs.

Taube's experiment has rate limiting electron transfer because Cr(II) (d^4, Jahn Teller ion) is substitutionally labile but...

replace Cr(II) with V(II) (d^3, inert) as $[V(H_2O)_6]^{2+}$ makes the **first step rate limiting**.

What is the effect of the nature of X^- in $[Co(NH_3)_5X]^{2+}$ likely to be if:
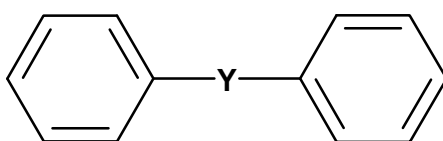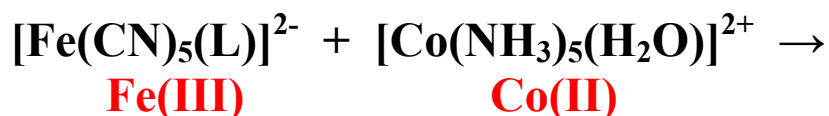
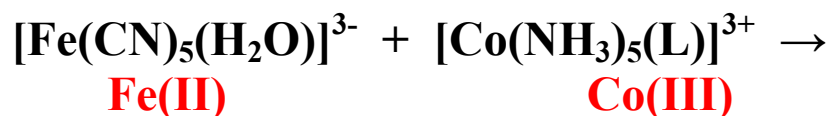   *a) step 1 is rate limiting?*

   very little effect since mostly affected by lability of leaving group on partner (assuming I_D mechanism is operative)

   b) step 2 is rate limiting?

   some effect because the stronger the bridge, the better electronic effects are transmitted:

   X- order: $F^- < Cl^- < Br^-, OH^- < I^-$

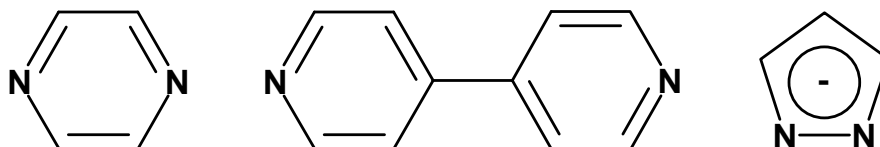**Electronic communication through the ligand is important:**

$[Fe(CN)_5(H_2O)]^{3-}$ + $[Co(NH_3)_5(L)]^{3+}$ →
    Fe(II)   Co(III)

$[Fe(CN)_5(L)]^{2-}$ + $[Co(NH_3)_5(H_2O)]^{2+}$ →
    Fe(III)   Co(II)

k depends on nature of Y:

large if Y = CH=CH, C(O), N, O (conjugated system)

small if Y = CH₂, CH₂CH₂ (saturated linkers)

In general, single atoms, small conjugated units like CN⁻ or SCN⁻ and larger conjugated π-systems facilitate electron transfer

Outer sphere mechanism

- **complexes are usually kinetically inert**

- **quantum mechanical 'tunneling' of e$^-$ between metals**

Self-exchange outer sphere redox rates (*from Table 26.9 text*)**:**

$$[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$$

M	n L	d^n, spin states	k (L mol^{-1} s^{-1})
Fe	3 bipy	d^5 ls, d^6 ls	>10^6
Os	3 bipy	d^5 ls, d^6 ls	>10^6
Co	3 phen	d^6 ls, d^7 hs	40
Fe	6 H$_2$O	d^5 hs, d^6 hs	3
Co	3 en	d^6 ls, d^7 hs	10^{-4}
Co	6 NH$_3$	d^6 ls, d^7 hs	10^{-6}

Considerations in an outer sphere mechanism:

1) **reactants must get close together for tunneling to occur**

   - **electrostatic repulsion slows rate**

2) **bond lengthening and shortening must occur**

   - **even though ΔG^0 must be zero in these reactions, individual M-L bonds must increase or decrease in length appropriate to the metal oxidation state (higher ox. st. results in shorter bonds in most cases)**

3) **Franck-Condon principle must be obeyed**

   - **electronic transitions (and electron transfer) occur on a far shorter timescale than molecular vibrations (nuclear motion)**

   - **this means that electron transfer will only occur when the complexes are distorted to the appropriate geometry for the products – i.e., this imposes an electronic barrier on the rate of electron transfer**

- as a result, the larger the bond length changes required, the larger the barrier and the slower the rate:

Eg. $[Co(NH_3)_6]^{2+/3+}$ is a change from low spin d^6 to high spin d^7 and the average Co-N distance changes from 1.96 Å (Co^{3+}) to 2.11 Å (Co^{2+}), plus there is a spin change required so the rate is very slow

Eg. $[Fe(bipy)_3]^{2+/3+}$ adds only one electron to a low spin d^5 configuration going to low spin d^6 (t_{2g}^5 to t_{2g}^6) and this results in small changes in bond lengths (1.96 to 1.97 Å) and rapid electron transfer rates

- π-bonding ligands have low lying empty MO's that facilitate intermolecular electron transfer as well:

Eg. Compare $[Co(phen)_3]^{2+/3+}$ and $[Co(NH_3)_6]^{2+/3+}$
Rate difference of about 10^7 in electron transfer caused by phen's ability to accept electrons and act as a kind of *'transfer station'* for electrons