Schedule

- Lecture 7: M-M bonds
  δ-bonds and bonding in metal clusters
- Lecture 8: Rates of reaction
  Ligand-exchange reactions, labile and inert metal ions
- Lecture 9: Redox reactions
  Inner and outer-sphere reactions

Summary of Last Lecture

Ligand substitution reactions

- Dissociative and associative mechanisms possible
- Rates vary widely for transition metal complexes
  - M^{3+} slower than M^{2+}
  - d^n with large LFSE are slow (d^3, d^8 and low spin d^{5-7})

Today's lecture

- e^- transfer reactions

Redox Reactions

- Redox reactions are very important in inorganic and bioinorganic chemistry. The shuttling of electrons between transition metal cations is at the centre of a wide variety of vital biological processes
- Redox reactions involving transition metal complexes generally occur *very rapidly:*
  - thermodynamics (using E^0 values) is very useful in predicting the outcome of reactions
- e^- transfer reactions appear to occur via two reaction mechanisms
  - outer sphere
  - inner sphere

Outer Sphere e⁻ Transfer

- The self-exchange reaction below is believed to occur via an outer sphere mechanism

$^*Fe(H_2O)_6^{2+}$ + $Fe(H_2O)_6^{3+}$ → $^*Fe(H_2O)_6^{3+}$ + $Fe(H_2O)_6^{2+}$ **ΔG = 0**

reductant oxidant

- The two complexes (the **reductant** and the **oxidant**):
  - diffuse together in solution to form **outer sphere** complex,
  - an electron is transferred from reductant to oxidant
  - the complexes diffuse apart
  - the ligands remain attached throughout the reaction

- Most redox reactions in biology occur via this mechanism
  - **Marcus theory** explains the rate of these reactions (1992 Nobel prize for Chemistry)

Outer Sphere e⁻ Transfer

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reductant oxidant

- e⁻ transfer occurs very rapidly – nuclei are too heavy to responds **the Franck-Condon principle**
- The products are formed with the geometries of the reactants
- After formation, they can relax to their true bond lengths

Outer Sphere e⁻ Transfer

- The products are formed with the geometries of the reactants:
  - ionic radii: Fe^{2+} (75 pm) > Fe^{3+} (69 pm)
  - **if** reactants are in their ground states, the products will be formed in **excited states**:

$^*[(H_2O)_5Fe{-}OH_2]^{2+}$ —e⁻ transfer→ $^*[(H_2O)_5Fe{-}OH_2]^{3+}$ **bonds too long**

$[(H_2O)_5Fe\text{-}OH_2]^{3+}$ —transfer→ $[(H_2O)_5Fe\text{-}OH_2]^{2+}$ **bonds too short**

↓ relax

$^*[(H_2O)_5Fe\text{-}OH_2]^{3+}$

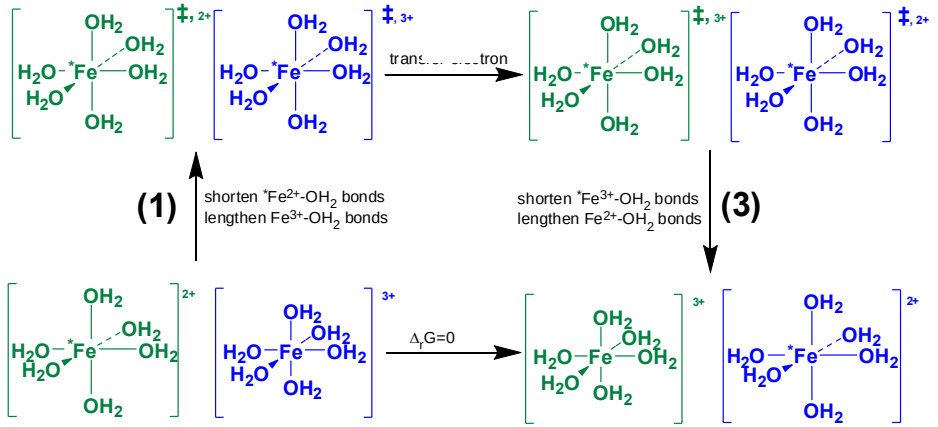
$[(H_2O)_5Fe{-}OH_2]^{2+}$

- These excited states will then relax, **releasing energy**
- **BUT ΔG = 0** so energy seems to have been created from nothing

REACTION CANNOT BE OCCURING FROM GROUND STATES

Outer Sphere e⁻ Transfer

- There is an activation step in which bonds in $Fe(H_2O)_5^{2+}$ are shortened and those in $Fe(H_2O)_6^{3+}$ are lengthened **so they are exactly the same**



- activation energy provided in (1) = relaxation energy in (3) so ΔG = 0

Outer Sphere e$^-$ Transfer

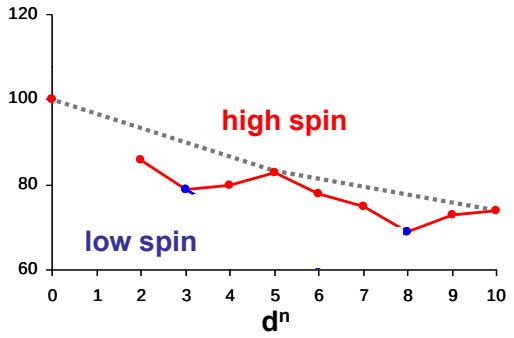
- The activation step involves making the bond lengths in oxidant and reductant the same:
  - ➢ if oxidant and reductant have very different bond lengths → activation energy is large → reaction is slow
  - ➢ if oxidant and reductant have similar bond lengths → activation energy is small → reaction is fast

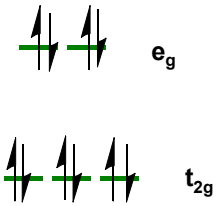
Need to compare bond lengths in oxidant and reductant to understand rate:

- Metals get smaller across period due to increasing *Z*
- Occupation of e_g^* orbitals lengthens bonds
- M^{3+} are smaller than M^{2+} due to charge

Ionic Radii - Recap

radii of M^{2+} ions (pm)





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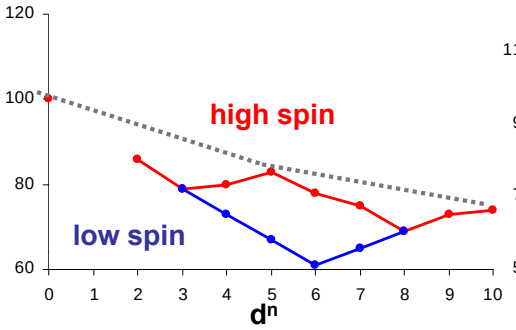
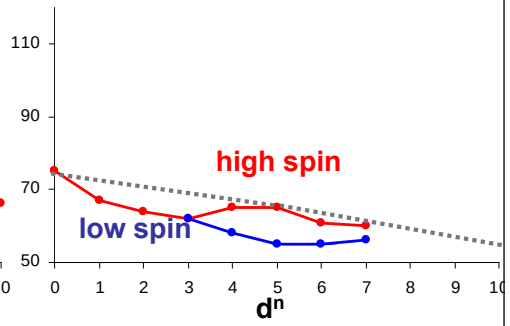


radii of M^{3+} ions (pm)



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metal ion pair	difference in M-O bond lengths	rate constant (M^{-1} s^{-1})
Fe^{2+}(aq) (d^6), Fe^{3+}(aq) (d^5)	13 pm	4
Cr^{2+}(aq) (d^4), Cr^{3+}(aq) (d^3)	18 pm	2×10^{-5}

Inner Sphere e$^-$ Transfer

- A different and *faster* mechanism operates **if**
  - either the oxidant or the reductant possesses a ligand capable of bonding to two metals at once ("bridging") AND
  - the other reactant is labile (able to exchange ligands

$$[Cr(H_2O)_6]^{2+} + [Co(H_2O)_5(Cl)]^{2+} \rightleftharpoons [(H_2O)_5Cr\text{-}Cl\text{-}Co(H_2O)_5]^{4+} + H_2O$$

inner-sphere complex

$$[(H_2O)_5Cr\text{-}Cl\text{-}Co(H_2O)_5]^{4+} \overset{e^- \text{ transfer}}{\rightleftharpoons} [(H_2O)_5Cr\text{-}Cl\text{-}Co(H_2O)_5]^{4+}$$

Cr(II)-Cl-Co(III) inner-sphere complex

Cr(III)-Cl-Co(II) inner-sphere complex

$$[(H_2O)_5Cr\text{-}Cl\text{-}Co(H_2O)_5]^{4+} \xrightarrow{+H_2O} [(H_2O)_5Cr\text{-}Cl]^{2+} + [Co(H_2O)_6]^{2+}$$

Inner Sphere e$^-$ Transfer

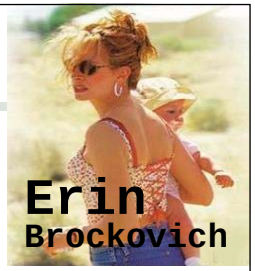
- The inner sphere reaction is possible as
  - Cl^- has >1 lone pair so can bond to Cr and Co in the inner-sphere complex
  - Cr^{2+} is labile (d^4 – Jahn-Teller distorted)

- Note that
  - once e$^-$ transfer has occurred, it is the Co^{2+} which is labile and Cr^{3+} is inert
  - therefore bridging ligand leaves with Cr^{3+}

$$[(H_2O)_5Cr\text{-}Cl\text{-}Co(H_2O)_5]^{4+} \xrightarrow{+H_2O} [(H_2O)_5Cr\text{-}Cl]^{2+} + [Co(H_2O)_6]^{2+}$$

Cr(III)-Cl-Co(II) inner-sphere complex

Toxicity of CrO_4^-



- CrO_4^- is a powerful oxidizing agent:

  $CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$ $E^0 = +0.6$ V

- It acts as a skin irritant due to oxidation of organic molecules
  - however, as reduction is a 3e$^-$ process, it is **metastable** as few organic oxidations involve 3 electrons

- It therefore passes through the skin
  - it has a very similar structure to SO_4^{2-} and is therefore "allowed" to pass through cell and nuclear membranes

- In the cell nucleus
  - it slowly reduces to Cr(III) (by oxidizing DNA or proteins)
  - Cr^{3+} binds to DNA and proteins causing mutations and cancers
  - Cr^{3+} (d^3) is inert so it is **very difficult** to remove

Summary

By now you should be able to....

- Explain that the key steps in the outer sphere mechanism
- Explain why the activation step involves the bond lengths in oxidant and reductant becoming the same
- Explain why and predict why the *difference* in oxidant and reductant bond lengths affects the rate
- Explain the key steps in the inner sphere mechanism
- Predict whether an e transfer mechanism can occur via the inner sphere mechanism by looking for the presence of a bridging ligand on one reactant and the lability of the other reactant

Practice

1. Explain the differences in the rate constants for the following self-exchange, electron transfer reactions:

   $[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$ $k = 4\ M^{-1}\ s^{-1}$

   $[Fe(bpy)_6]^{2+} + [Fe(bpy)_6]^{3+} \rightarrow [Fe(bpy)_6]^{3+} + [Fe(bpy)_6]^{2+}$ $k > 10^6\ M^{-1}\ s^{-1}$

   $[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$ $k = 10^{-6}\ M^{-1}\ s^{-1}$

   (Hint: bpy = bipyridyl, a strong-field ligand, $[Co(NH_3)_6]^{3+}$ is diamagnetic).

2. The rate of reduction of $[Co(NH_3)_5(H_2O)]^{3+}$ by $Cr^{2+}(aq)$ is seven orders of magnitude slower than reduction of its conjugate base, $[Co(NH_3)_5(OH)]^{3+}$ by $Cr^{2+}(aq)$. The rates of the reduction of the same cobalt complexes by $[Ru(NH_3)_6]^{2+}$ differ by only a factor of 10.

   Explain these observations.

   (Hint: OH^- is able to bridge)

Summary of Course – week 4

Ligand-field ('d-d') spectroscopy

- be able to predict/explain number of bands for d^1-d^9 (high-spin)
- be able to calculate Δ_{oct} for d^1, d^3, d^4, d^6, d^7, d^8 and d^9
- be able to explain differences in band intensity (spin forbidden, orbitally forbidden, Laporte forbidden)
- be able to explain the appearance of charge transfer transitions
- be able to explain and predict the occurance of the Jahn-Teller effect and its consequences (structural, spectroscopic, reaction rates)

Resources

- Slides for lectures 1-4
- Shriver and Atkins "Inorganic Chemistry" Chapter 9 (4^{th} Edition)
- Housecroft and Sharpe "Inorganic Chemistry" Chapter 20.6-7 (2^{nd} Edition)

Summary of Course – week 5

Complexes of π-acceptor ligands

- be able to explain synergic (σ-donation, π-back donation) model for bonding in M-CO and M-N_2 complexes
- be able to explain reduction in CO stretching frequency in complex
- be able to explain changes in CO stretching frequency with metal charge and with ligands
- electron counting in CO, N_2 and NO complexes: 18 e^- rule

Resources

- Slides for lectures 5-6
- Shriver and Atkins "Inorganic Chemistry" Chapter 21.1-5, 21.18 (4^{th} Edition)
- Housecroft and Sharpe "Inorganic Chemistry" Chapter 23.2 (2^{nd} Edition)

Summary of Course – week 6

Metal-metal bonding

- be able to predict bond order for M_2L_x dimers using d-electron count and σ, π and δ molecular orbital diagram
- be able to predict bond order in larger metal-halide clusters using d-electron count shared over edges of cluster
- be able to predict bond order in metal carbonyl clusters using 18 e^- rule

Reaction mechanisms

- be able to describe ligand exchange mechanisms
- be able to explain role of metal charge and LFSE in rate of ligand exchange
- be able to describe electron transfer reaction mechanisms
- be able to predict relative rate of outer sphere reaction for different metals

Resources

- Slides for lectures 7-9
- Shriver and Atkins "Inorganic Chemistry" Chapter 18.11, 21.20, 20.1-20.13
- Housecroft and Sharpe "Inorganic Chemistry" Chapter 23.6, 25