Class 9.3

Redox Chemistry IV - Electron Transfer Processes

Friday, October 31
CHEM 462
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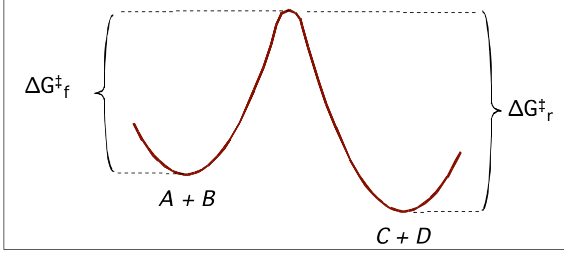
Outer Sphere Electron transfer

- The mechanisms whereby electrons are transferred in redox reactions have been under intense scrutiny and have generated 2+ Nobel prizes.
- We will start with a discussion of “outer-sphere” degenerate electron transfers (those involving transfer between oxidized and reduced forms of the same couple). See Sec. 6.5 in text.

Transition state theory expression for the rate constant, k:

$k = \left({}^{k_B T}/_{hc}\right) e^{-\Delta G^{\ddagger}/RT} = A e^{-\Delta G^{\ddagger}/RT}$ c = *conc.*

or $\ln k = \ln A - {}^{\Delta G^{\ddagger}}/_{RT}$ $\left({}^{k_B T}/_{h} \approx 6 \times 10^{12}\right)$



Some rate constants ($M^{-1}\ s^{-1}$)

	k
$[Cr(H_2O)_6]^{2+} + [Cr(H_2O)_6]^{3+} \rightarrow Cr^{III} + Cr^{II}$	2×10^{-5}
$[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \rightarrow Ru^{III} + Ru^{II}$	8×10^{2}
$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow Co^{III} + Co^{II}$	$\sim 10^{-9}$
$[Fe(bpy)_3]^{2+} + [Fe(bpy)_6]^{3+} \rightarrow Fe^{III} + Fe^{II}$	$> 10^{6}$
$[IrCl_6]^{3-} + [IrCl_6]^{2-} \rightarrow Ir^{IV} + Ir^{III}$	$> 10^{6}$
$[Co(H_2O)_6]^{2+} + [Co(H_2O)_6]^{3+} \rightarrow Co^{III} + Co^{II}$	~ 5

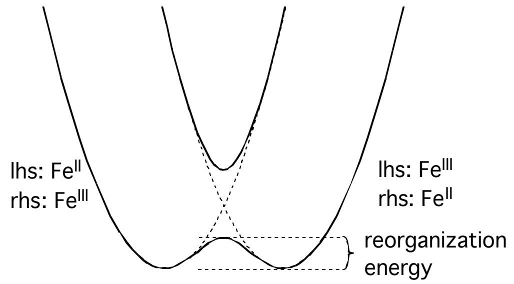
All but the last of these is "easily" explained!

Note: All these rxns involve at least one d^6 or d^3 (substitutionally inert) complex.

t_{2g}^6 $\quad$ t_{2g}^5

$[Fe^{II}(bpy)_3]^{2+} + [Fe^{III}(bpy)_3]^{3+} \rightarrow$
$[Fe^{III}(bpy)_3]^{3+} + [Fe^{II}(bpy)_3]^{2+}$

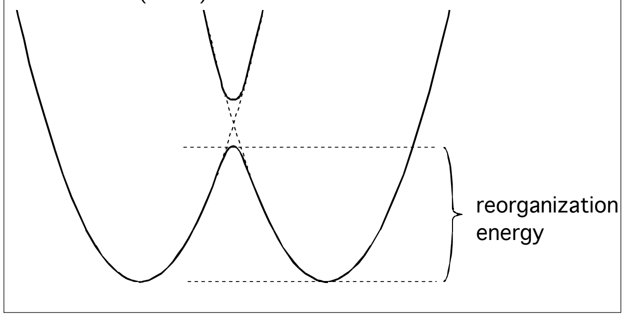
d(Fe–N) = 1.96 Å $\quad$ 1.97 Å



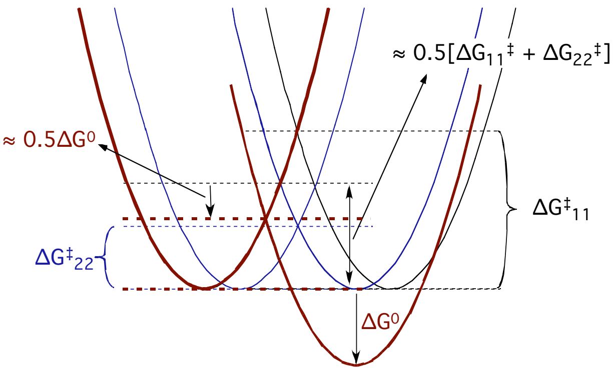
$t_{2g}^5e_g^2$ $\quad$ t_{2g}^6

$[Co^{II}(NH_3)_6]^{2+} + [Co^{III}(NH_3)_6]^{3+} \rightarrow$
$[Co^{III}(NH_3)_6]^{3+} + [Co^{II}(NH_3)_6]^{2+}$

d(Co–N) = 2.11 Å $\quad$ 1.96 Å

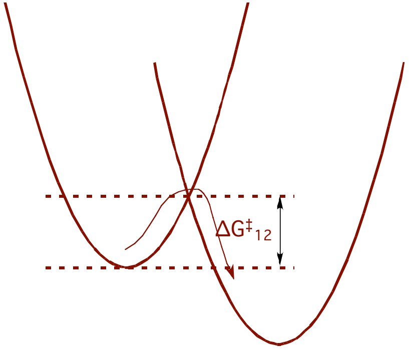


Outer Sphere Cross Reactions



Outer Sphere Cross Reactions

$\Delta G_{12}^{\ddagger} \approx 0.5[\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger} + \Delta G^0]$



Marcus (Nobel, 1992) Theory

$$\Delta G_{12}^{\ddagger} \approx 0.5[\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger} + \Delta G^0]$$

From absolute rate theory,

$$k = Ae^{-\Delta G^{\ddagger}/RT} \quad \text{or} \quad \ln k = \ln A - {}^{\Delta G^{\ddagger}}/_{RT}$$

comparing to the first eqn:

$$\ln k_{12} = {}^{1}/_{2}\{\ln f + \ln k_{11} + \ln k_{22} + \ln K_{eq}\}$$

$$k_{12} = [f \times k_{11} \times k_{22} \times K_{eq}]^{1/2};$$

$f \approx 1$ (contains all the prefactors)

Inner Sphere Reactions

- Electron transfer between metal complexes sometimes involve more than tunneling of electrons from one complex to another.
- In 1953, Taube (Nobel 1983) performed classic experiments that unequivocally demostrated cases electron transfer occurs through an intervening (shared) ligand.

Taube's Experiments

$$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_3O^+ \rightarrow [Cr(H_2O)_5X]^{2+} + [Co(H_2O)_6]^{2+} + 5NH_4^+$$

X = halides, SCN^-, N_3^-, $RCOO^-$, etc

[Note: Both Co^{III} (d^6) and Cr^{III} (d^3) complexes undergo very slow ligand exchange reactions. In general, d^3 , d^4 (low-spin), d^5 (low-spin), d^6 (low-spin) exchange ligands slowly (< 1 min^{-1}).

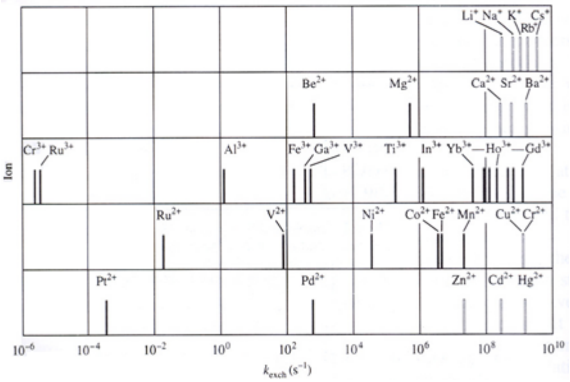
Some rate constants (M^{-1} s^{-1})

$[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+} \rightarrow Co^{II} + Cr^{III}$ $k = 8 \times 10^{-5}$

$[CoX(NH_3)_5]^{2+} + [Cr(NH_3)_6]^{3+} \rightarrow Co^{II} + Cr^{III}$

X	*k*
F^-	2.5×10^5
Cl^-	6.0×10^5
I^-	3.0×10^6
NCS^-	19
SCN^-	1.9×10^5
H_2O	0.1

Water Exchange rates



Water Exchange Rates

- For alkali and alkaline earth, dissociative mechanism seems to hold throughout.

rates increase with ionic size

⇑⇓

M-OH_2 bonds weaken with increasing ion size

⇑⇓

M-OH_2 bonds break in transition state

M^{III} ions: $Sc^{3+} < Y^{3+} < La^{3+}$

$Al^{3+} < Ga^{3+} < In^{3+}$

Mechanistic Clues

- Activation parameters: $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$
  - How are each of these measured?
- For dissociative reactions, we expect that all of these will be > 0.

Trends for T.M.s

V^{2+}, Ni^{2+} > Co^{2+} > Cr^{2+}, Cu^{2+} > Fe^{2+} > Mn^{2+}, Zn^{2+}

Does this LFSE trend correlate
with exchange rates?

$\Delta V^{\ddagger} > 0$ for Fe^{2+}, Co^{2+}, Ni^{2+}

but, $\Delta V^{\ddagger} < 0$ for V^{2+}, Mn^{2+}

Co^{3+}, Rh^{3+}, Ir^{3+}, Cr^{3+} all quite inert - all have high LFSE's

Associative vs. Dissociative

$\Delta V^{\ddagger}$ measurements indicate mechanisms may differ in seemingly similar reactions:

$$[Co(NH_3)_5(H_2O)]^{3+} + Cl^- \rightarrow [Co(NH_3)_5Cl]^{2+} + H_2O$$
$$\Delta V^{\ddagger} = 1.4 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$$

$$[Rh(NH_3)_5(H_2O)]^{3+} + Cl^- \rightarrow [Rh(NH_3)_5Cl]^{2+} + H_2O$$
$$\Delta V^{\ddagger} = 3.0 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$$

$$[Cr(NH_3)_5(H_2O)]^{3+} + Cl^- \rightarrow [Cr(NH_3)_5Cl]^{2+} + H_2O$$
$$\Delta V^{\ddagger} = -4.9 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$$