Chem 241

Lecture 17

Announcement

March 10 → LGRT 0323
March 26 → Second Exam

Homework

Start reading chapter 5

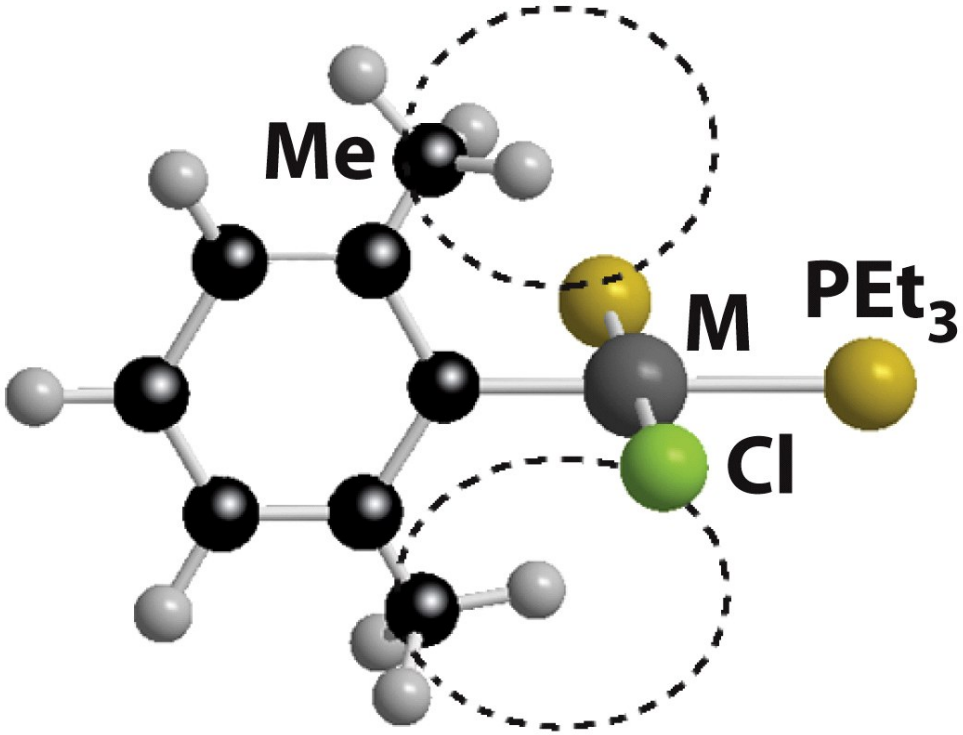
Chapter 20
Exercises: 1, 2, 3, 6, 8, 10, 11, 12 and 19

Recap

Kinetic definitions
Mechanisms
Trans Effect

Steric Effects

Steric crowding usually hinders associative attacks.



6

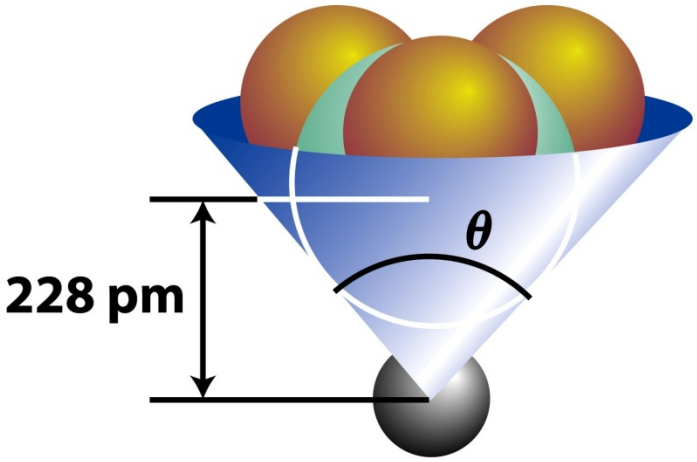
Structure 20-6

Tolman Cone Angle

Approximating the ligand as a cone.

Table 20.9 Tolman cone angles for various ligands

Ligand	$\theta/^\circ$	Ligand	$\theta/^\circ$
CH_3	90	$P(OC_6H_5)_3$	127
CO	95	PBu_3	130
Cl, Et	102	PEt_3	132
PF_3	104	η^5-C_5H_5(Cp)	136
Br, Ph	105	PPh_3	145
I, $P(OCH_3)_3$	107	η^5-C_5Me_5 (Cp*)	165
PMe_3	118	2,4-$Me_2C_5H_3$	180
t-Butyl	126	$P(t\text{-}Bu)_3$	182

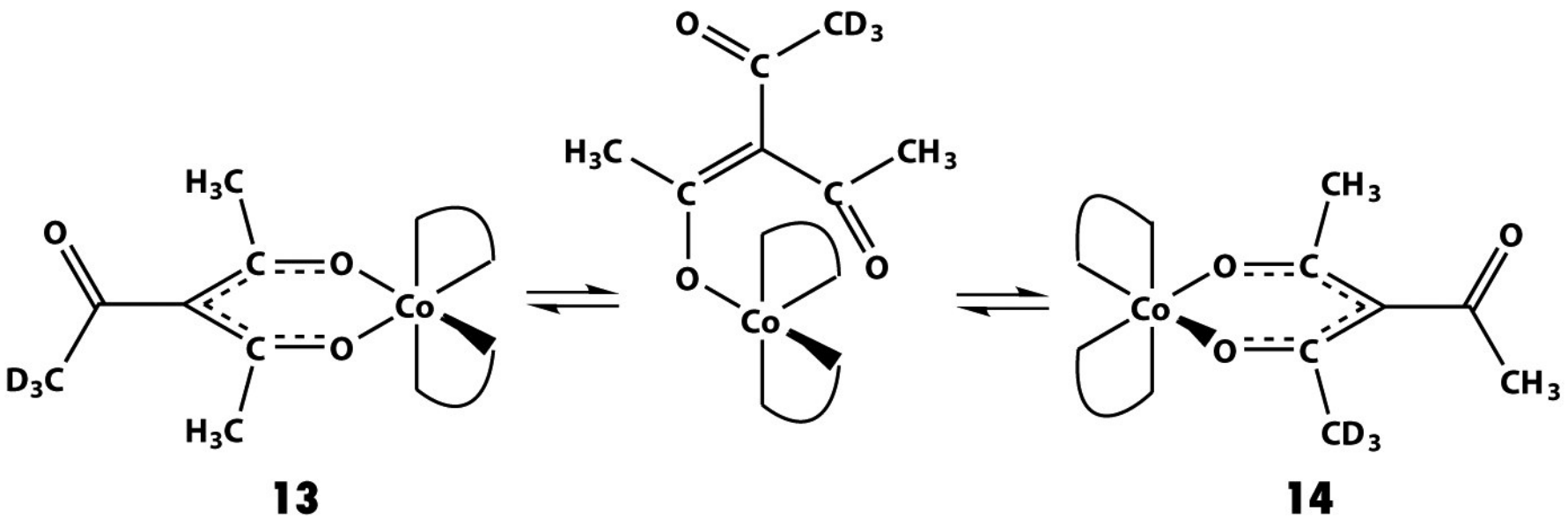


Isomerization

Go by a dissociative mechanism:

Bailer twist

Ray- Dust twist



Redox Reactions

Reduction – Electron Gain
Oxidation – Electron Loss

Reducing Agent – Species that supplies electrons
Oxidizing Agent – Species that removed electrons

Groups 1 and 2 will do oxidation states of +1 and +2, respectively. While some d metals like Os can go from 0 to +8

Redox Half Reactions

Reduction – Electron Gain

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

Oxidation – Electron Loss

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$

$Ag^{+}(aq) + e^{-} + Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-} + Ag(s)$

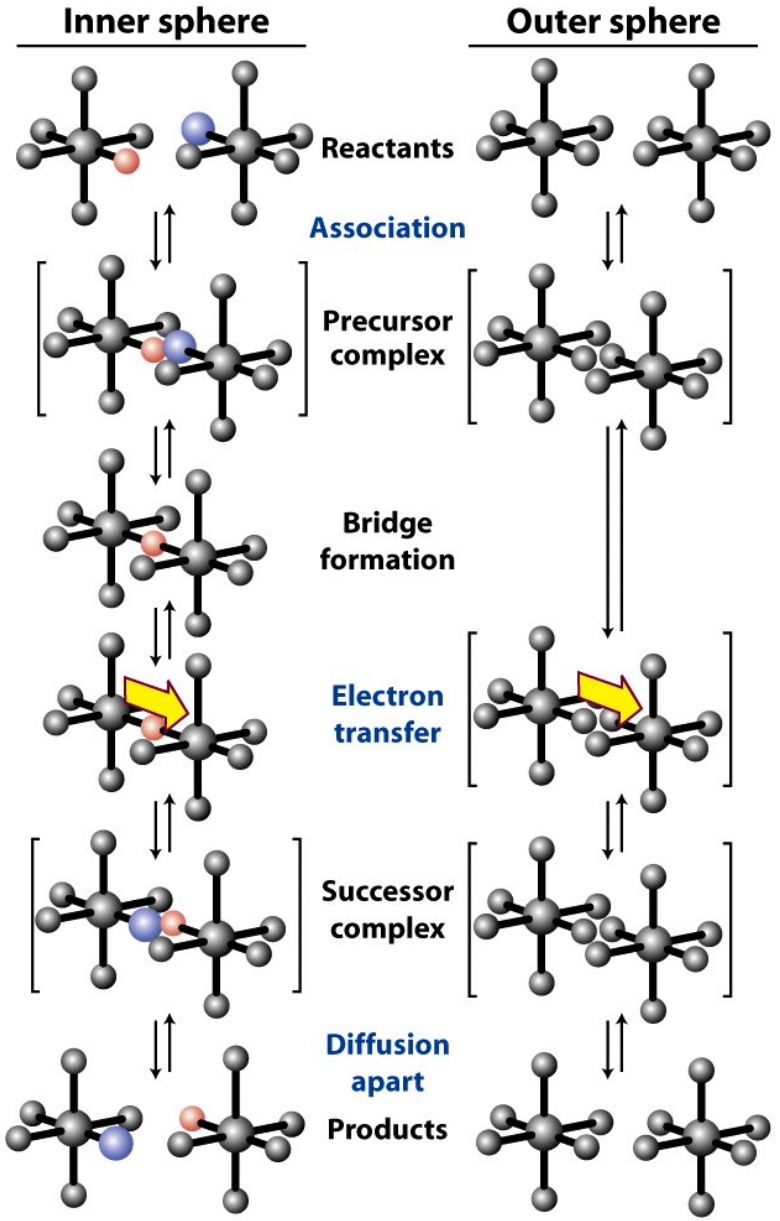
$2Ag^{+}(aq) + 2e^{-} + Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-} + 2Ag(s)$

$2Ag^{+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

Redox Mechanisms

$[CoCl(NH_3)_5]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow$
$[Co(NH_3)_5(H_2O)]^{2+} + [CrCl(H_2O)_5]^{2+}$

$[M(H_2O)_6]^{n+1} + [M(H_2O)_6]^{n} \rightarrow$
$[M(H_2O)_6]^{n} + [M(H_2O)_6]^{n+1}$



Photochemical Reactions

$[Cr(NH_3)_6]^{3+} + H_2O + h\nu \rightarrow [Cr(NH_3)_5(H_2O)]^{3+} + NH_3$

Sometimes not so simple:

$[Co^{III}Cl(NH_3)_5]^{2+} + H_2O + h\nu \rightarrow [Co^{II}(NH_3)_5(H_2O)]^{2+} + Cl\cdot$

$[Co^{II}(NH_3)_5(H_2O)]^{2+} + Cl\cdot \rightarrow [Co^{III}(NH_3)_5(H_2O)]^{3+} + Cl^-$

Quantum Yeild (Φ) – is the number of defined events, in terms of reactant or product, that occur per photon ansorbed by the system.

Photochemical Reactions

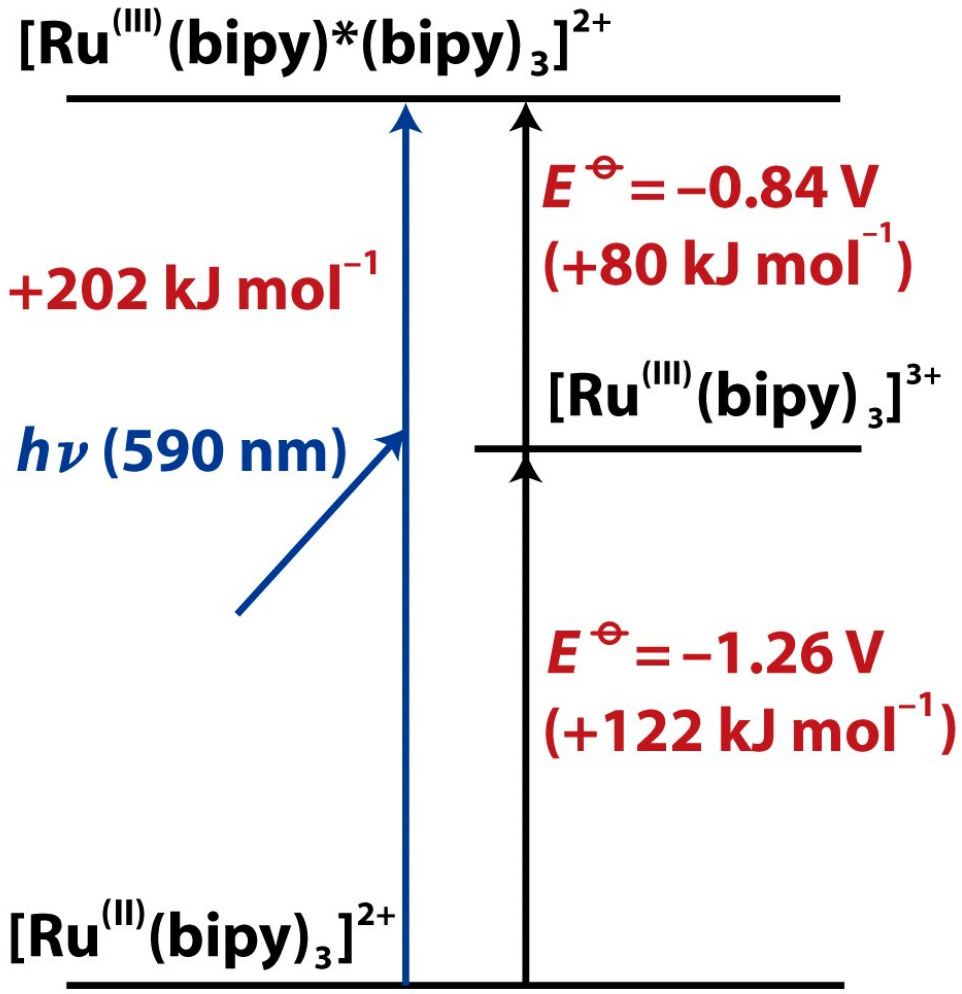
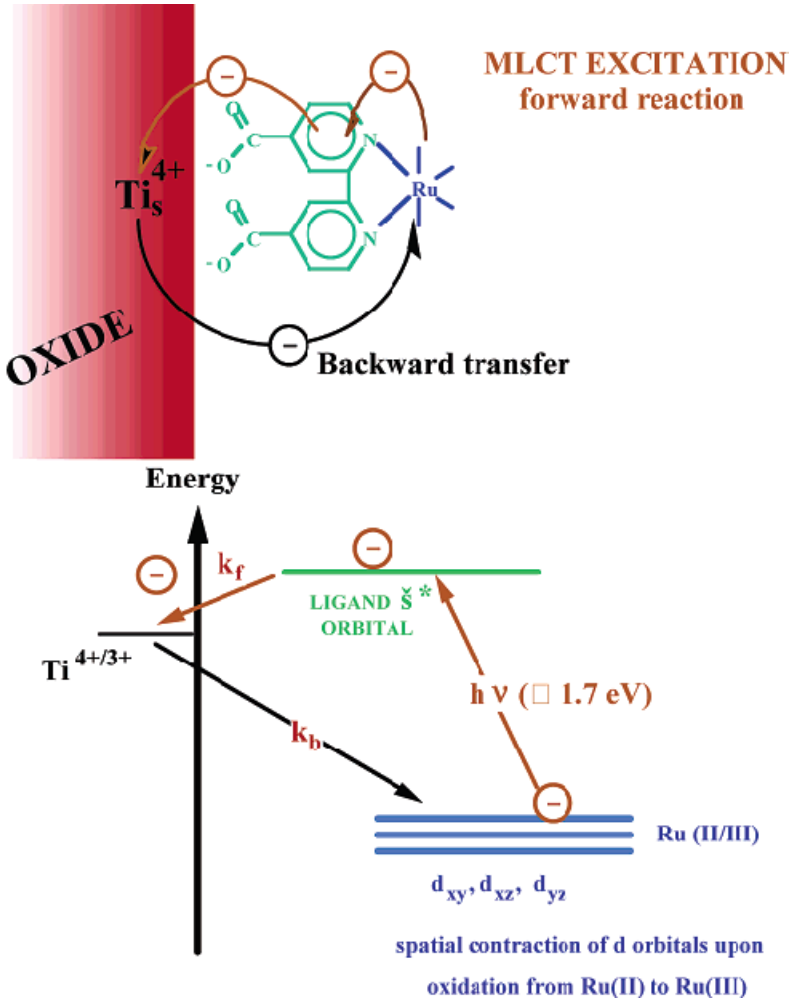


Figure 20-23
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Graetzel Cell



"…the supply of energy from the sun to the earth is gigantic, i.e., 3×10^{24} J year^{-1} or about 10^4 times more than what mankind consumes currently. In other words, covering only 0.1% of the earth's surface with solar cells with an efficiency of 10% would suffice to satisfy our current needs."

Standard Cell Potenial

$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $\quad E^{o} = 0.799\ V$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $\quad E^{o} = -0.337\ V$

$2Ag^{+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ $\quad E^{o} = 0.462$

$\Delta G^{o} = -nFE^{o}$ $\quad F = 96.48\ kC\ mol^{-1}$

Nernst Equation:

$$E = E^{0} - \frac{RT}{nF} InQ$$

Standard Cell Potenial

$$[H_2VO_4]^-(aq) + 4\ H^+(aq) + e^- \rightarrow VO_2^+(aq) + 3\ H_2O(l)$$

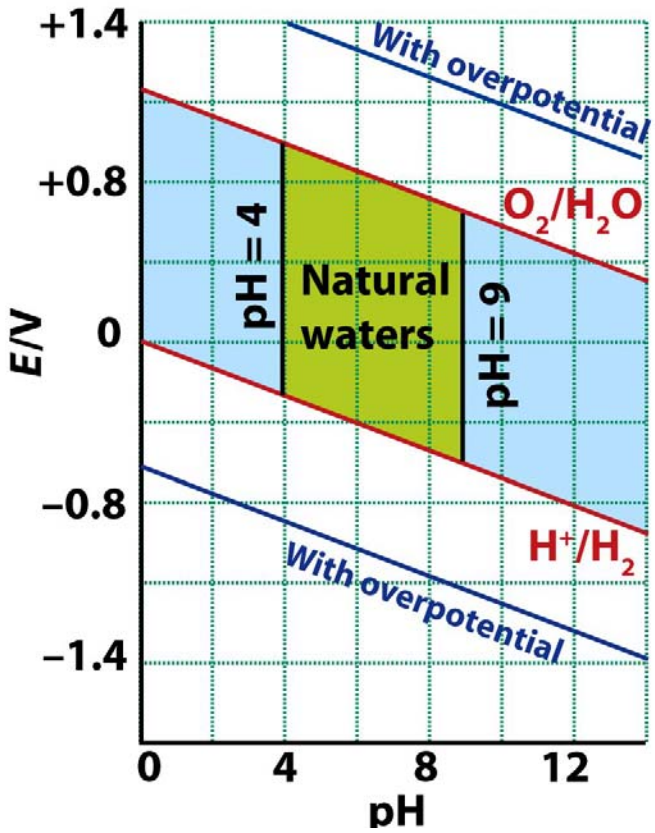
$$VO_2^+(aq) + 2\ H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$$

$$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$$

Solvent

$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-$

$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$



$M(s) + nH^+(aq) \rightarrow M^{n+} + n/2\ H_2(g)$

$4\ Fe^{2+}(aq) + O_2 + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l)$

Reactions with itself

Disproportionation: a redox reaction in which the oxidation number of an element is simultaneously raised and lowered.

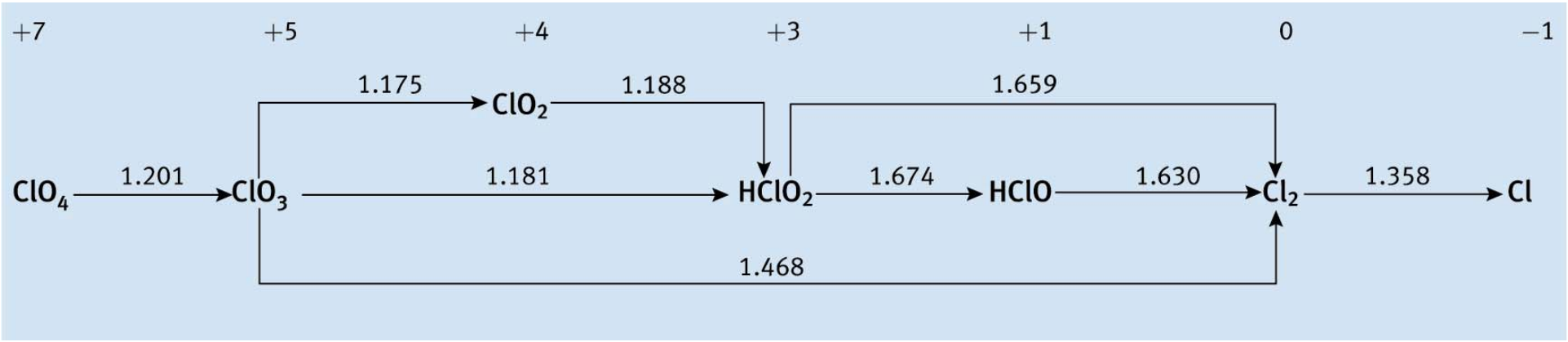
$2\ Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

$$Cu^{+}(aq) + e^{-} \rightarrow Cu(s) \qquad E = 0.52\ V$$
$$Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + e^{-} \qquad E = -0.16V$$

Comproportionation: a redox reaction in which two species of the same element in different oxidation states form a product in which the element is in the same oxidation state,

$$Ag^{2+}(aq) + Ag(s) \rightarrow 2Ag^{+}(aq) \quad E = 1.18\ V$$

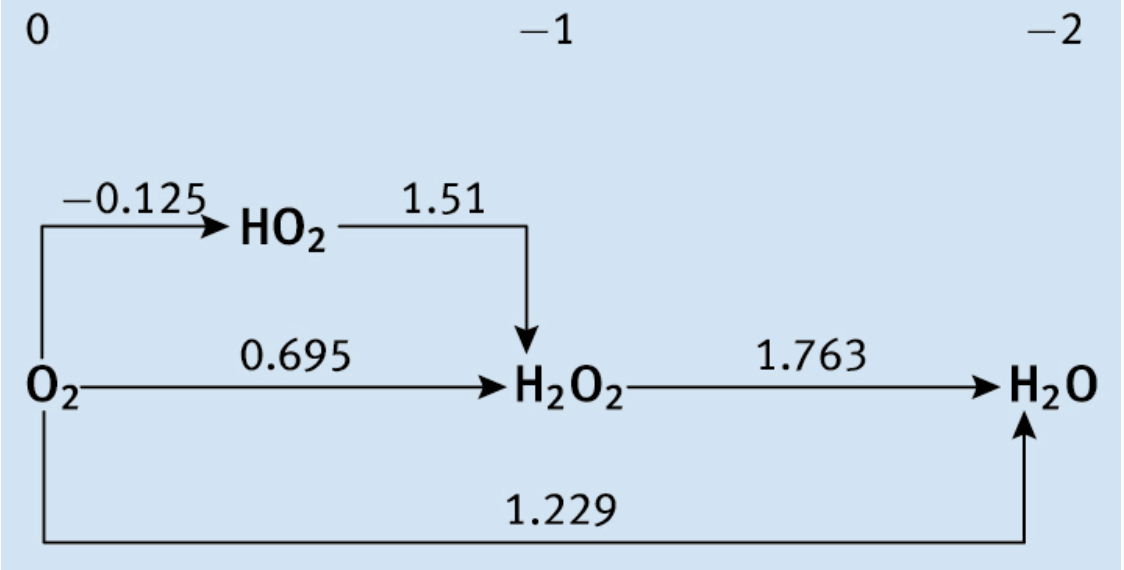
Latimer Diagram



$ClO_4^-(aq) + 2H^+(aq) + 2e^- \rightarrow ClO_3^-(aq) + H_2O(l)$

$$E^0(a+b) = \frac{n_a E^0(a) + n_b E^0(b)}{n_a + n_b}$$

Latimer Diagram



$2H^+(aq) + 2e^- + H_2O_2(aq) \rightarrow H_2O \quad E_{Right} = 1.76V$

$O_2 + H^+(aq) + 2e^- \rightarrow H_2O_2(aq) \quad E_{Left} = 0.70V$

$E_{Right} > E_{Left}$: Then reaction will be spontaneous, species tend to disproportionate.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$