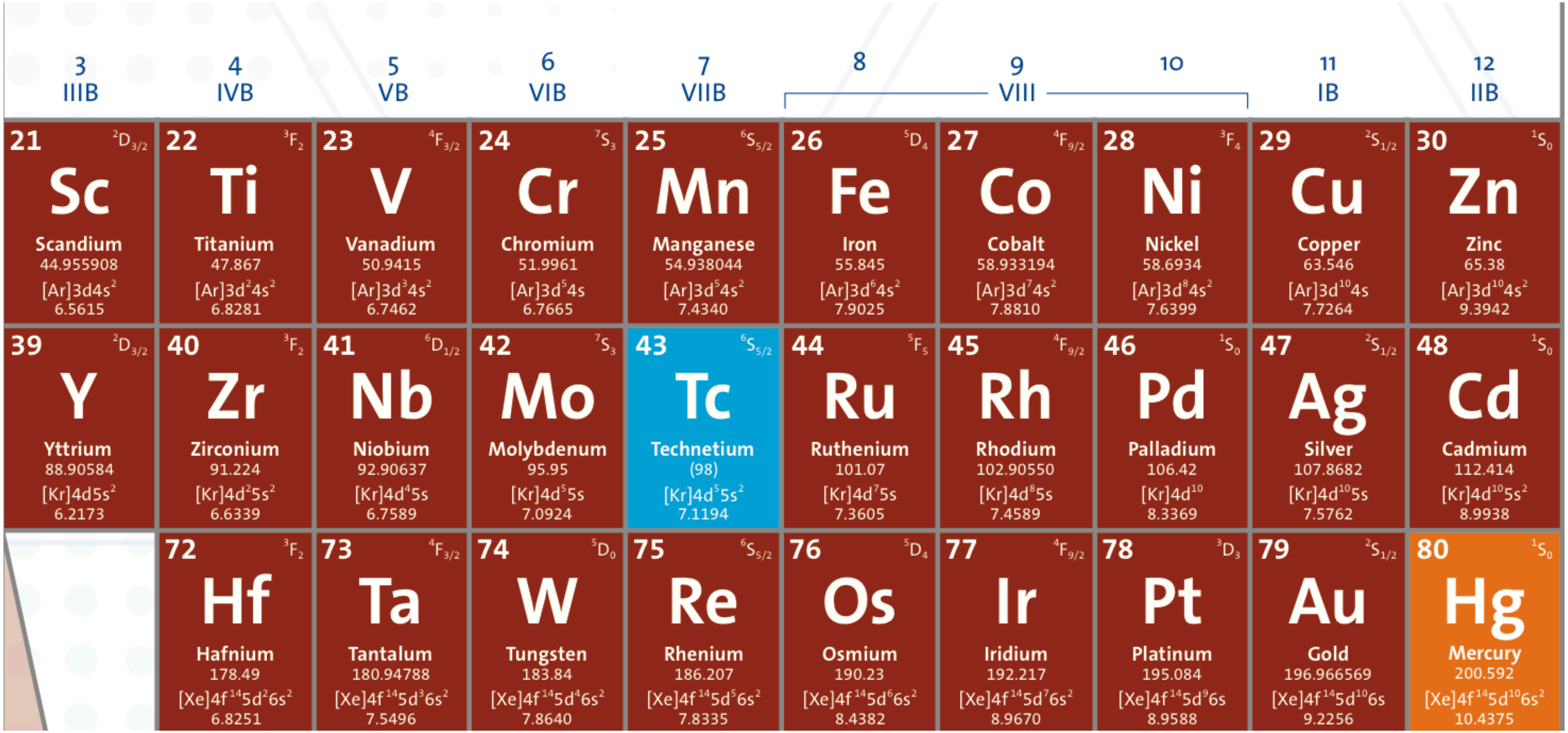
University of St Andrews

CH3514

Physical Inorganic Chemistry

CH3514

Dr Eli Zysman-Colman



3	4	5	6	7	8	9	10	11	12
IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB
21 $^{2}D_{3/2}$ **Sc** **Scandium** 44.955908 $[Ar]3d4s^{2}$ 6.5615	22 $^{3}F_{2}$ **Ti** **Titanium** 47.867 $[Ar]3d^{2}4s^{2}$ 6.8281	23 $^{4}F_{3/2}$ **V** **Vanadium** 50.9415 $[Ar]3d^{3}4s^{2}$ 6.7462	24 $^{7}S_{3}$ **Cr** **Chromium** 51.9961 $[Ar]3d^{5}4s$ 6.7665	25 $^{6}S_{5/2}$ **Mn** **Manganese** 54.938044 $[Ar]3d^{5}4s^{2}$ 7.4340	26 $^{5}D_{4}$ **Fe** **Iron** 55.845 $[Ar]3d^{6}4s^{2}$ 7.9025	27 $^{4}F_{9/2}$ **Co** **Cobalt** 58.933194 $[Ar]3d^{7}4s^{2}$ 7.8810	28 $^{3}F_{4}$ **Ni** **Nickel** 58.6934 $[Ar]3d^{8}4s^{2}$ 7.6399	29 $^{2}S_{1/2}$ **Cu** **Copper** 63.546 $[Ar]3d^{10}4s$ 7.7264	30 $^{1}S_{0}$ **Zn** **Zinc** 65.38 $[Ar]3d^{10}4s^{2}$ 9.3942
39 $^{2}D_{3/2}$ **Y** **Yttrium** 88.90584 $[Kr]4d5s^{2}$ 6.2173	40 $^{3}F_{2}$ **Zr** **Zirconium** 91.224 $[Kr]4d^{2}5s^{2}$ 6.6339	41 $^{6}D_{1/2}$ **Nb** **Niobium** 92.90637 $[Kr]4d^{4}5s$ 6.7589	42 $^{7}S_{3}$ **Mo** **Molybdenum** 95.95 $[Kr]4d^{5}5s$ 7.0924	43 $^{6}S_{5/2}$ **Tc** **Technetium** (98) $[Kr]4d^{5}5s^{2}$ 7.1194	44 $^{5}F_{5}$ **Ru** **Ruthenium** 101.07 $[Kr]4d^{7}5s$ 7.3605	45 $^{4}F_{9/2}$ **Rh** **Rhodium** 102.90550 $[Kr]4d^{8}5s$ 7.4589	46 $^{1}S_{0}$ **Pd** **Palladium** 106.42 $[Kr]4d^{10}$ 8.3369	47 $^{2}S_{1/2}$ **Ag** **Silver** 107.8682 $[Kr]4d^{10}5s$ 7.5762	48 $^{1}S_{0}$ **Cd** **Cadmium** 112.414 $[Kr]4d^{10}5s^{2}$ 8.9938
	72 $^{3}F_{2}$ **Hf** **Hafnium** 178.49 $[Xe]4f^{14}5d^{2}6s^{2}$ 6.8251	73 $^{4}F_{3/2}$ **Ta** **Tantalum** 180.94788 $[Xe]4f^{14}5d^{3}6s^{2}$ 7.5496	74 $^{5}D_{0}$ **W** **Tungsten** 183.84 $[Xe]4f^{14}5d^{4}6s^{2}$ 7.8640	75 $^{6}S_{5/2}$ **Re** **Rhenium** 186.207 $[Xe]4f^{14}5d^{5}6s^{2}$ 7.8335	76 $^{5}D_{4}$ **Os** **Osmium** 190.23 $[Xe]4f^{14}5d^{6}6s^{2}$ 8.4382	77 $^{4}F_{9/2}$ **Ir** **Iridium** 192.217 $[Xe]4f^{14}5d^{7}6s^{2}$ 8.9670	78 $^{3}D_{3}$ **Pt** **Platinum** 195.084 $[Xe]4f^{14}5d^{9}6s$ 8.9588	79 $^{2}S_{1/2}$ **Au** **Gold** 196.966569 $[Xe]4f^{14}5d^{10}6s$ 9.2256	80 $^{1}S_{0}$ **Hg** **Mercury** 200.592 $[Xe]4f^{14}5d^{10}6s^{2}$ 10.4375

Physical Inorganic Chemistry
CH3514

Dr Eli Zysman-Colman

Rm 244 in Purdie

eli.zysman-colman@st-andrews.ac.uk

http://www.zysman-colman.com/courses/ch3514_2017aut_en.php

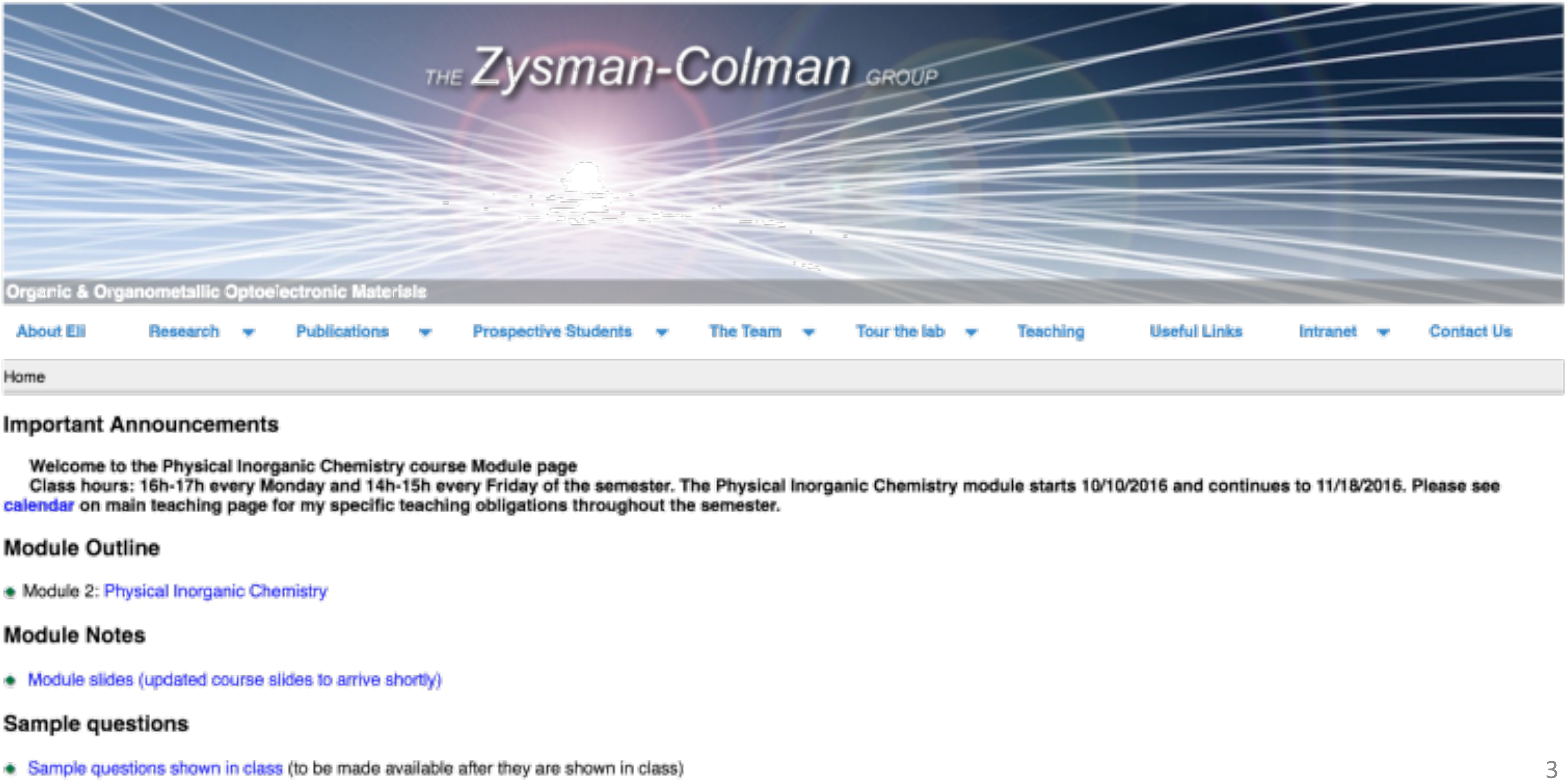
Physical Inorganic Chemistry
CH3514

Dr Eli Zysman-Colman

Rm 244 in Purdie

eli.zysman-colman@st-andrews.ac.uk

http://www.zysman-colman.com/courses/ch3514_2017aut_en.php



Important Announcements

Welcome to the Physical Inorganic Chemistry course Module page
Class hours: 16h-17h every Monday and 14h-15h every Friday of the semester. The Physical Inorganic Chemistry module starts 10/10/2016 and continues to 11/18/2016. Please see calendar on main teaching page for my specific teaching obligations throughout the semester.

Module Outline

- Module 2: Physical Inorganic Chemistry

Module Notes

- Module slides (updated course slides to arrive shortly)

Sample questions

- Sample questions shown in class (to be made available after they are shown in class)

Physical Inorganic Chemistry
CH3514

Dr Eli Zysman-Colman

Rm 244 in Purdie

eli.zysman-colman@st-andrews.ac.uk

http://www.zysman-colman.com/courses/ch3514_2017aut_en.php

Course Outline

Physical Chemistry and Bonding of Transition Metals

Aims: A continuation of the chemistry of the 3d transition metals with particular focus on the thermodynamics, bonding and kinetics of reactions.

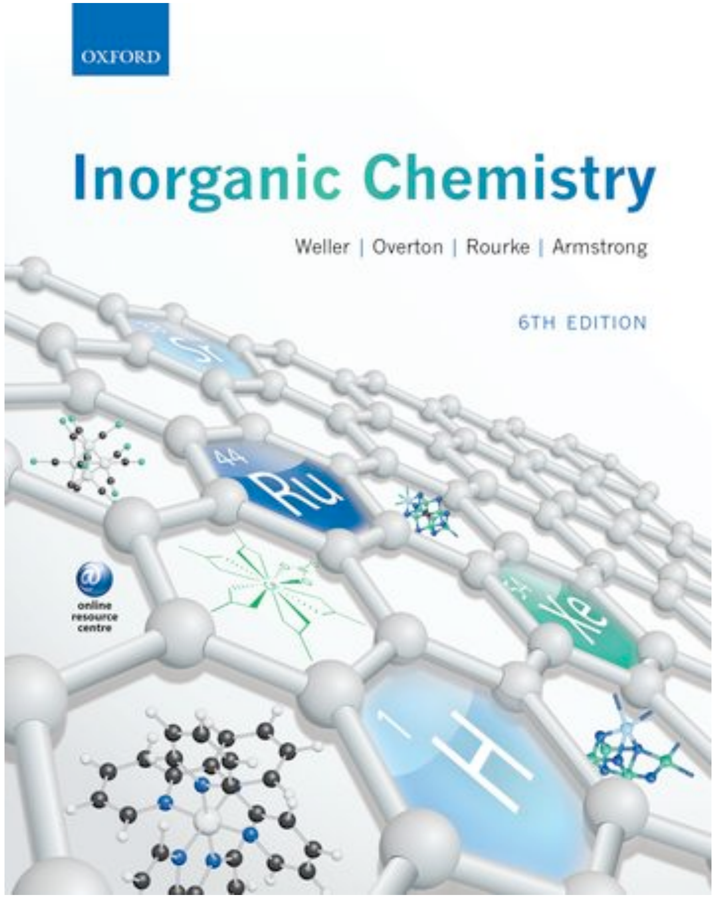
Course Outline

Physical Chemistry and Bonding of Transition Metals

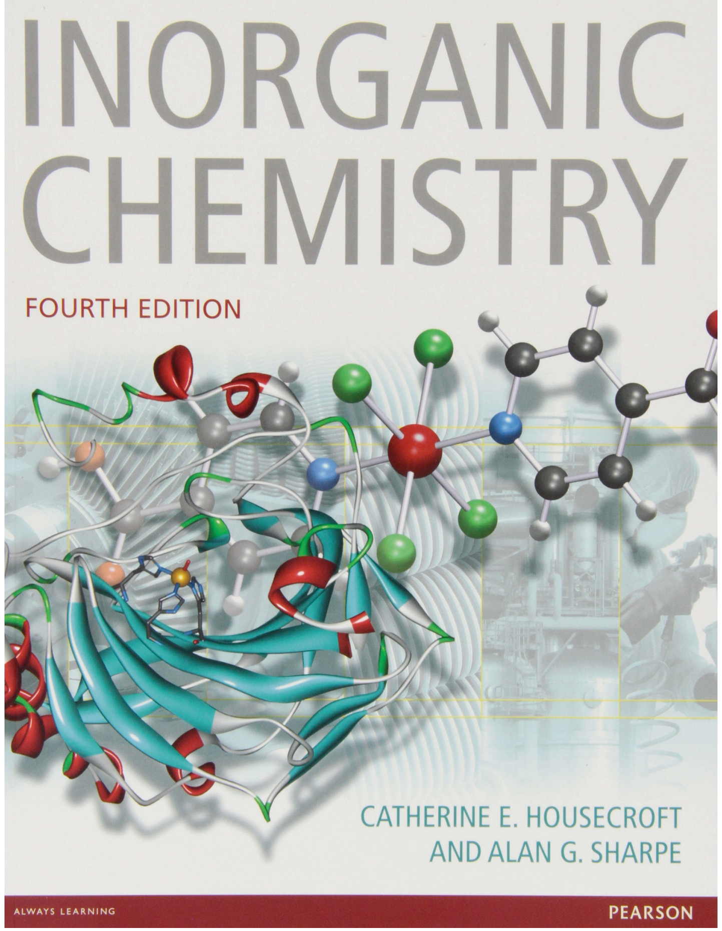
Objectives:

- A summary of how d-orbitals affect the properties of the transition metals.
- To understand metal ion-ligand complexation equilibria; stepwise formation and overall stability constants. Relationship of β_{ML} to K_{ML} and ΔG^o_{ML}
- To understand the trends in β_{ML} across the period Sc – Zn and the Irving Williams maximum at Cu^{2+} due to Jahn-Teller effect at d^9
- To understand how molecular orbital theory can be used to explain the properties of metal-ligand complexes
- To understand the origins of the chelate effect – the increase in β_{ML} with chelate ligands. To appreciate and rationalise the entropic and enthalpic factors involved – trends across the period. Correlation of K_n (β_n) values with LFSE.
- To appreciate that thermodynamic stability and kinetic lability are independent phenomena – not necessarily correlated. Equilibrium can be rapidly obtained irrespective of the size of K.
- To appreciate the range of labilities on 3d aqua metal ions and the correlation with LFSE. Definition of the terms inert and labile. Correlation of inertness with high LFAE – linked to LFSE.

Resource Books



Inorganic Chemistry, 6th Edition
Mark Weller, Tina Overton,
Jonathan Rourke and Fraser Armstrong



Inorganic Chemistry, 4th Edition
Catherine Housecroft and Alan Sharpe

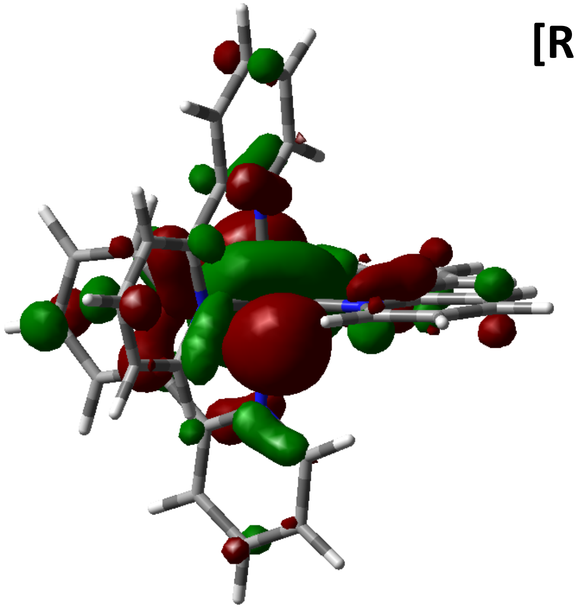
Frontier MO's of σ-Donor, π-Donor and π-Acceptor Ligands

Before we can understand MO diagrams and bonding in complexes, we must understand the nature of the frontier MOs of ligands.

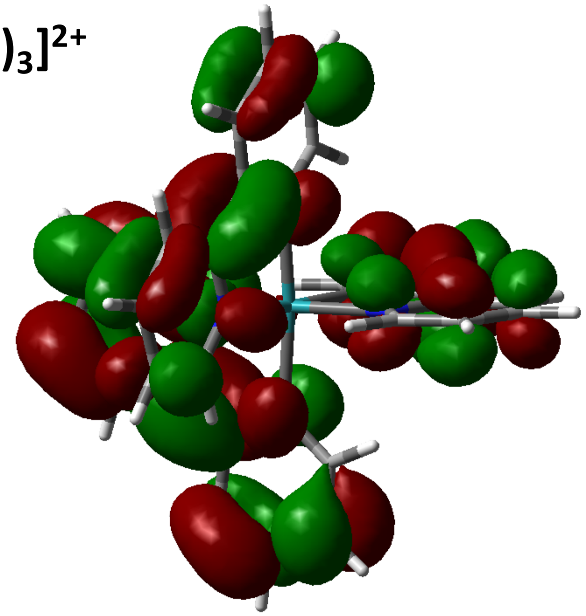
There are three types of orbital interactions between ligands and metals, which define the ligand type:

- σ-donors
- π-donors
- π-acceptors

[Ru(bpy)$_3$]$^{2+}$



HOMO



LUMO

University of St Andrews

CH3514

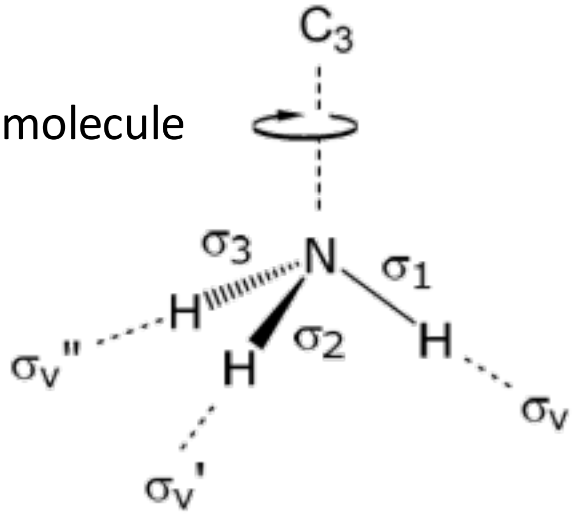
Frontier MO's of σ-Donor Ligands

These ligands donate two e⁻s from an orbital of σ-symmetry:

Examples include: H^-, CH_3^-, NR_3, PR_3, OH_2.

Let's look at NH_3 in more detail as an example of a molecular ligand (as opposed to a simple atomic ligand)

There are 3 N-H σ-bonds in this molecule and it has C_3 symmetry



Frontier MO’s of σ-Donor Ligands

These ligands donate two e⁻s from an orbital of σ-symmetry:

Examples include: H^-, CH_3^-, NR_3, PR_3, OH_2.

Let’s look at NH_3 in more detail as an example of a molecular ligand (as opposed to a simple atomic ligand)

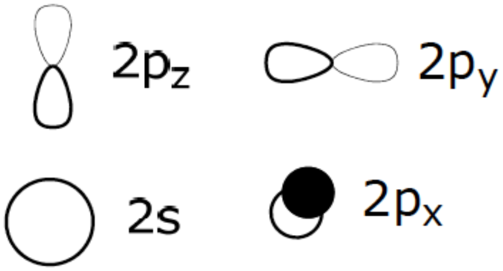
Let’s analyze the Symmetry Adapted Linear Combinations (SALC) more closely.

3 H’s

No nodes

1 node

N



a_1

e

Recall that only orbitals of the same symmetry can combine to form new Linear Combinations of Atomic Orbitals (LCAO)

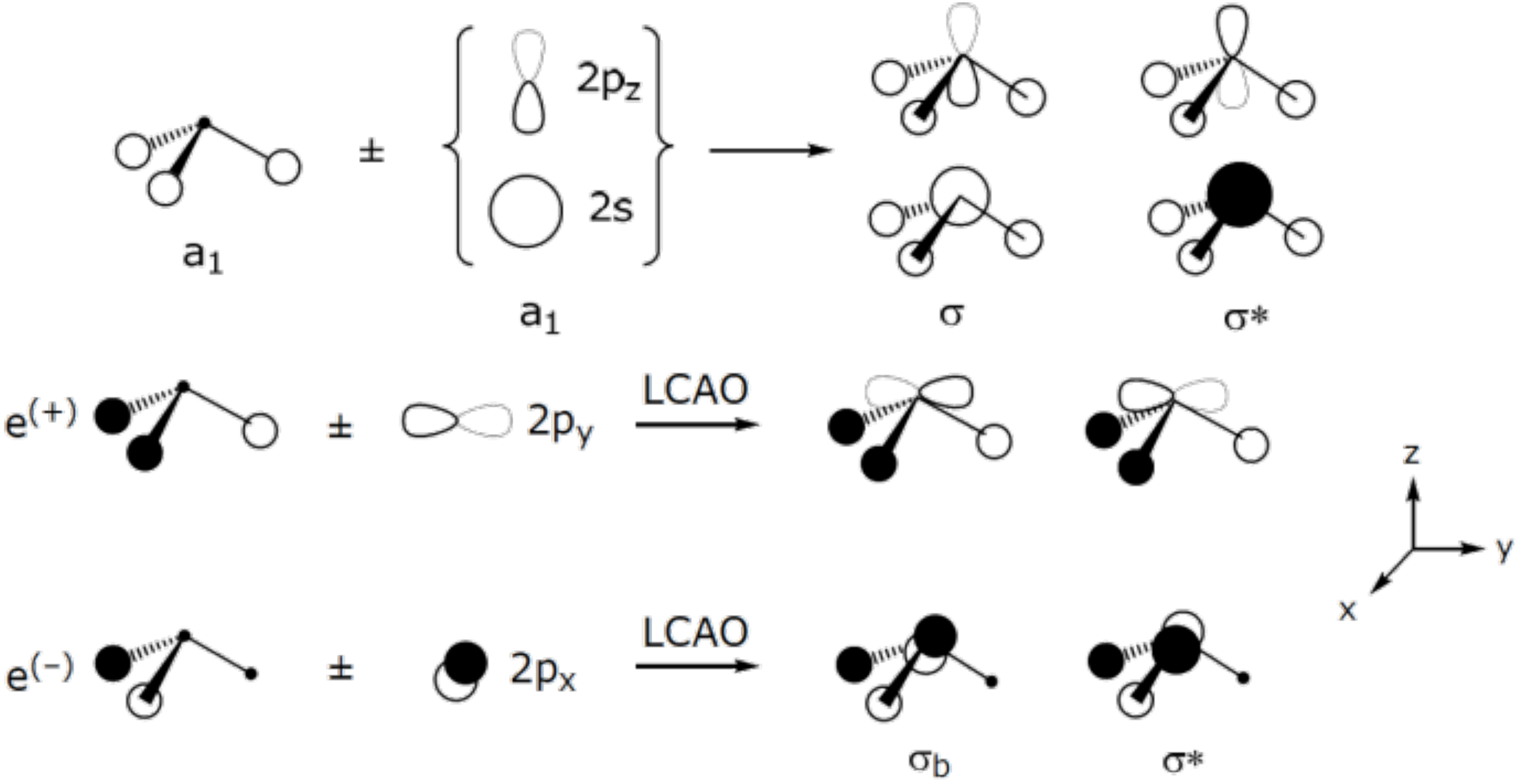
Frontier MO's of σ-Donor Ligands

These ligands donate two e^-s from an orbital of σ-symmetry:

Examples include: H^-, CH_3^-, NR_3, PR_3, OH_2.

Let's look at NH_3 in more detail as an example of a molecular ligand (as opposed to a simple atomic ligand)

Let's determine the Linear Combinations of Atomic Orbitals (LCAO)s



Frontier MO's of σ-Donor Ligands

Let's look at NH_3 in more detail as an example of a molecular ligand (as opposed to a simple atomic ligand)

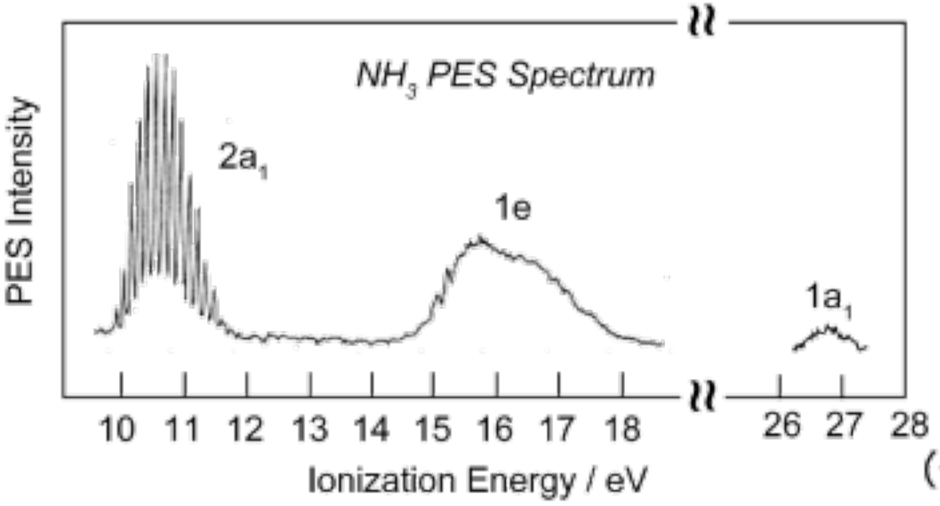
Let's now look at the MO diagram

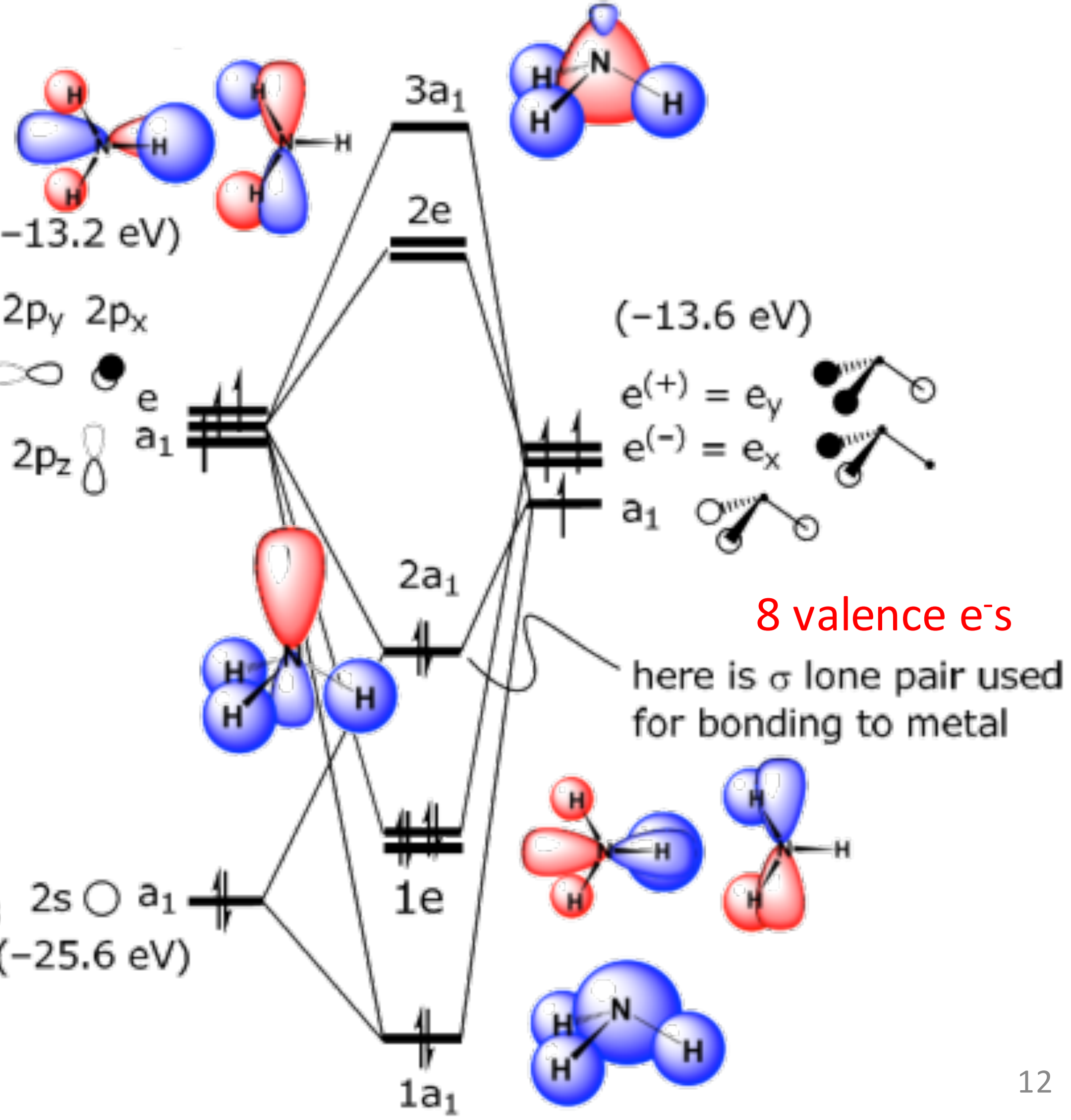
Remember:

- The greater the overlap, the greater the splitting
- The closer in energy between the two sets of orbitals, the greater the splitting

Note:

- The HOMO is used for bonding to the metal and it is the lone pair on N in a σ-orbital
- MO diagram predicts MOs of 3 different energies, which is borne out by PES



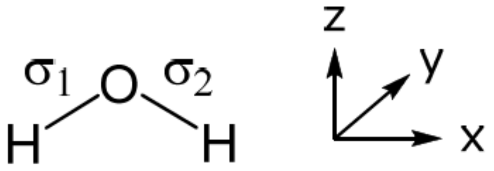


8 valence e^-s

here is σ lone pair used for bonding to metal

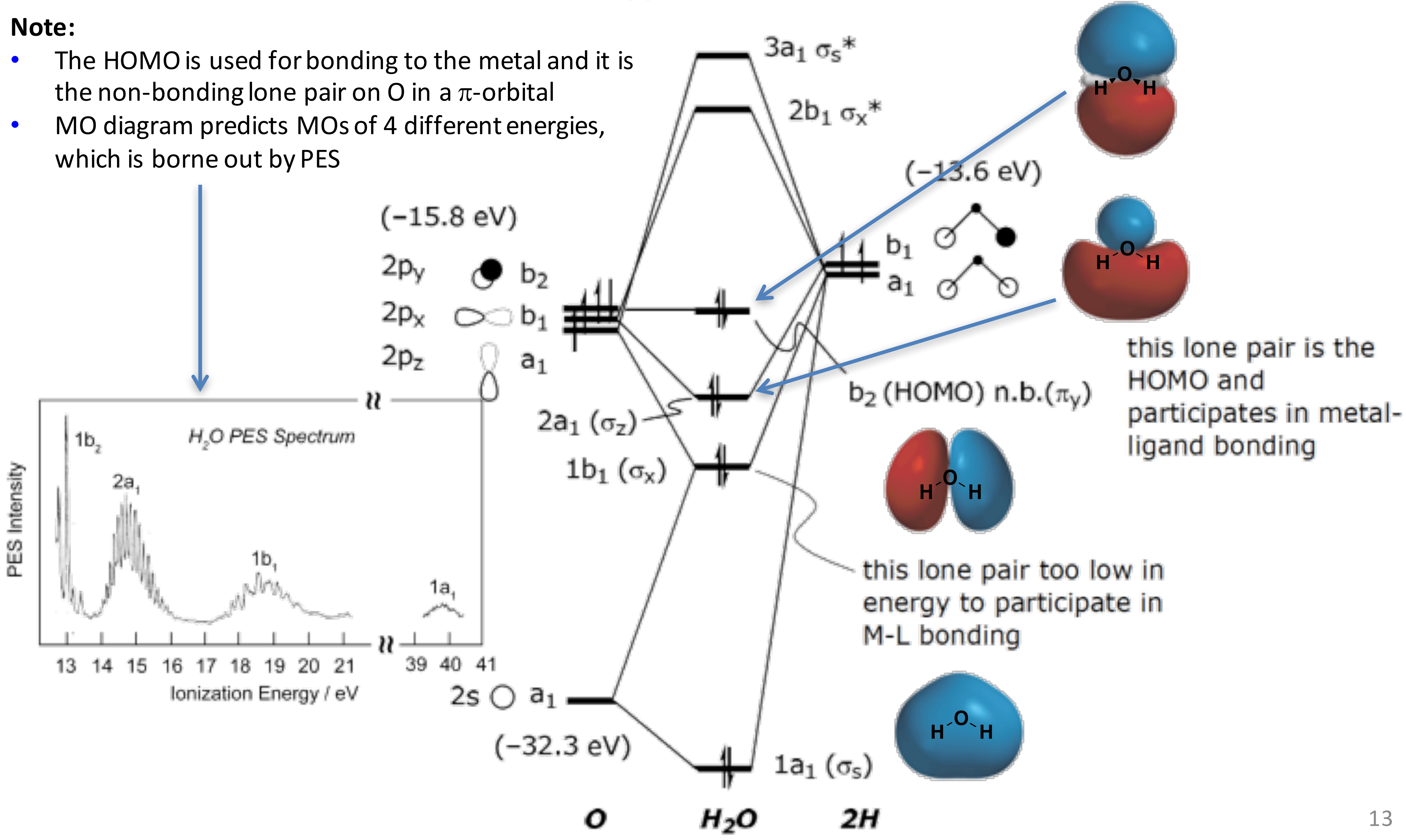
Frontier MO's of σ-Donor Ligands

How about H_2O with its 2 lone pairs?



Note:

- The HOMO is used for bonding to the metal and it is the non-bonding lone pair on O in a π-orbital
- MO diagram predicts MOs of 4 different energies, which is borne out by PES



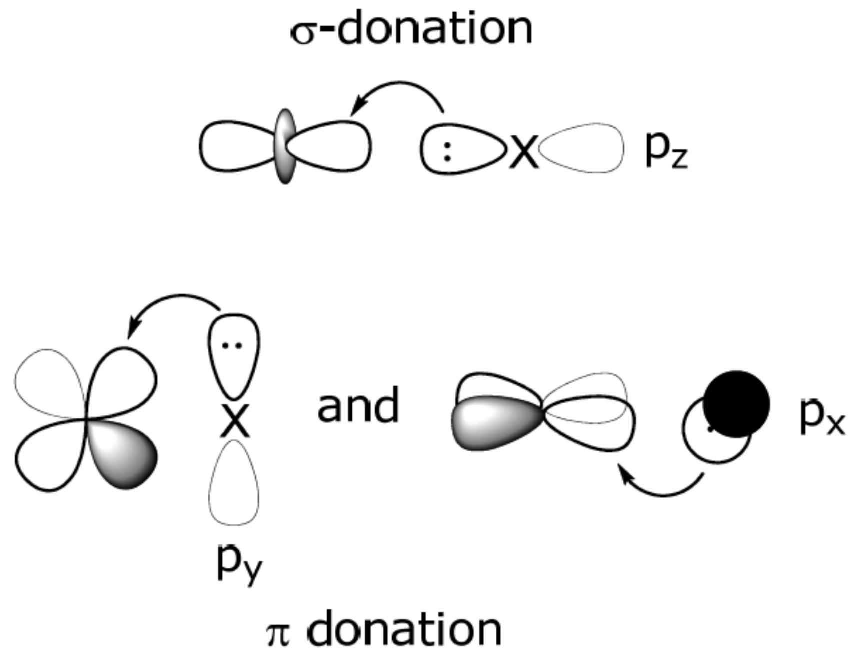
this lone pair is the HOMO and participates in metal-ligand bonding

this lone pair too low in energy to participate in M-L bonding

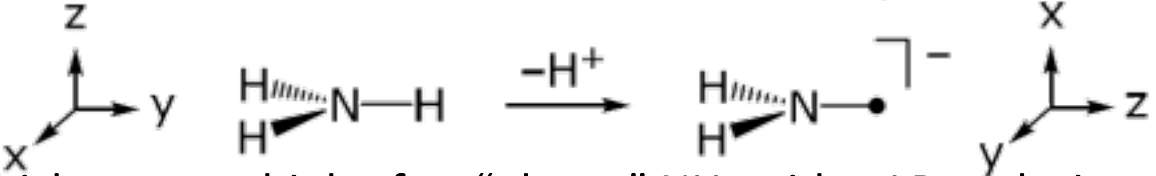
Frontier MO's of π-Donor Ligands

In addition to donating electron density to a metal via a σ-bond, e⁻s may be provided to the metal via a π-symmetry interaction.

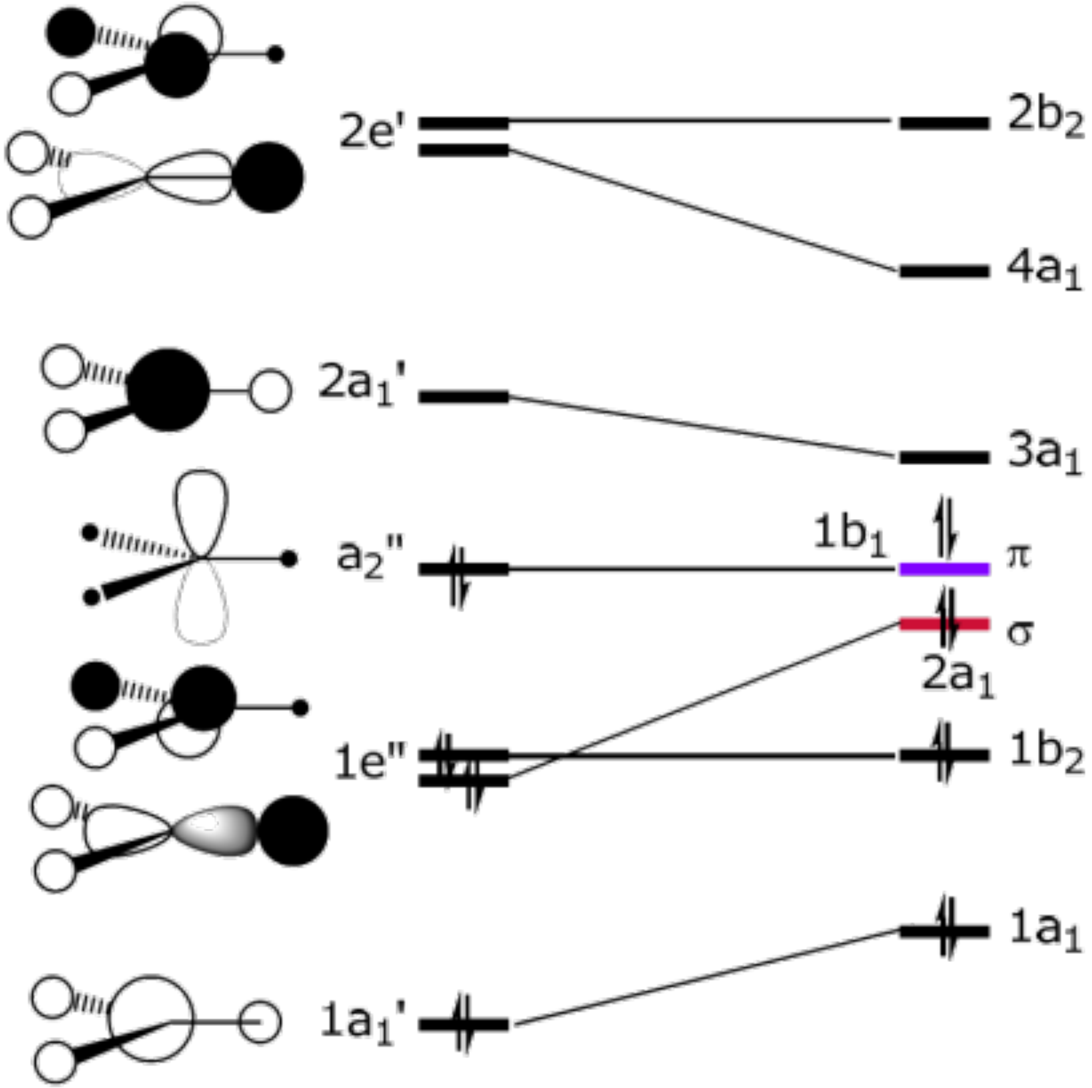
π-donor ligands include X^- (halide), amide (NR_2^-), sulfide (S^{2-}), oxide (O^{2-}), alkoxide (RO^-) η^3-C_3H_5, η^5-C_5H_5, η^6-C_6H_6



Frontier MO's of π-Donor Ligands

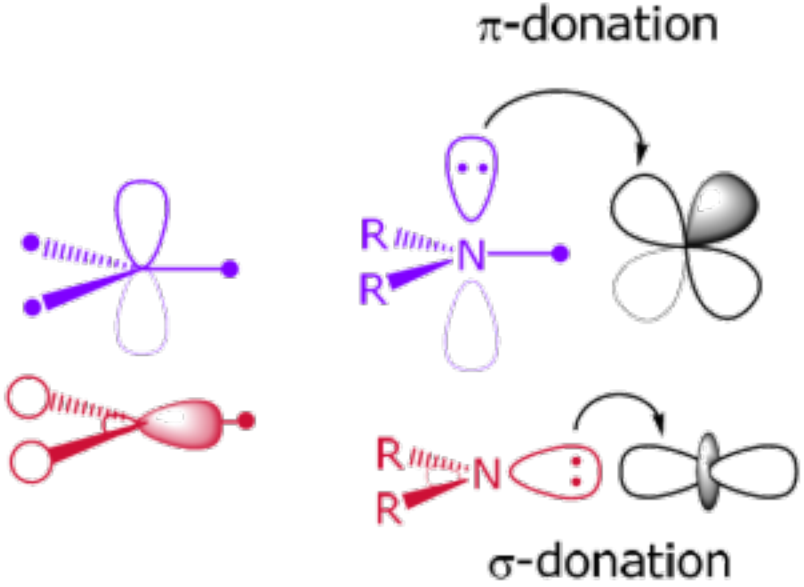


Let's look at NH_2^-, which we can think of as "planar" NH_3 with a LP replacing one of the H atoms



There are now 2 extra e-s compared to NH_3

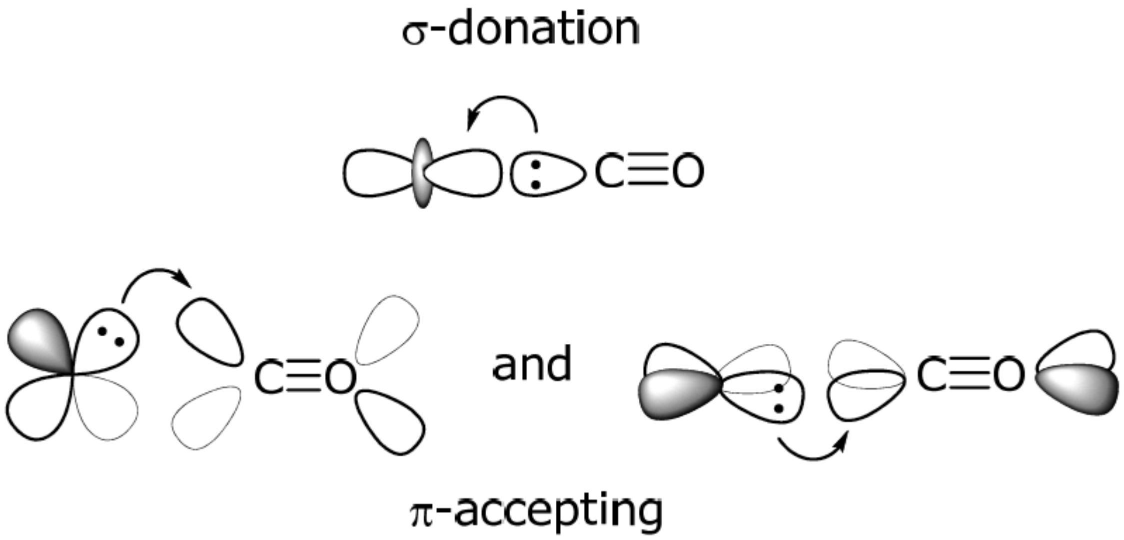
the HOMO is filled and of π-symmetry



Frontier MO's of π-Acceptor Ligands

This class of ligands donates e⁻s from a σ orbital
and these ligands accept e⁻s from the metal into an empty π* orbital.

CO is the archetype of this ligand class.
Other π-acceptors are NO^+, CN^-, CNR, H_2, C_2H_4, N_2, O_2, PR_3, BR_2



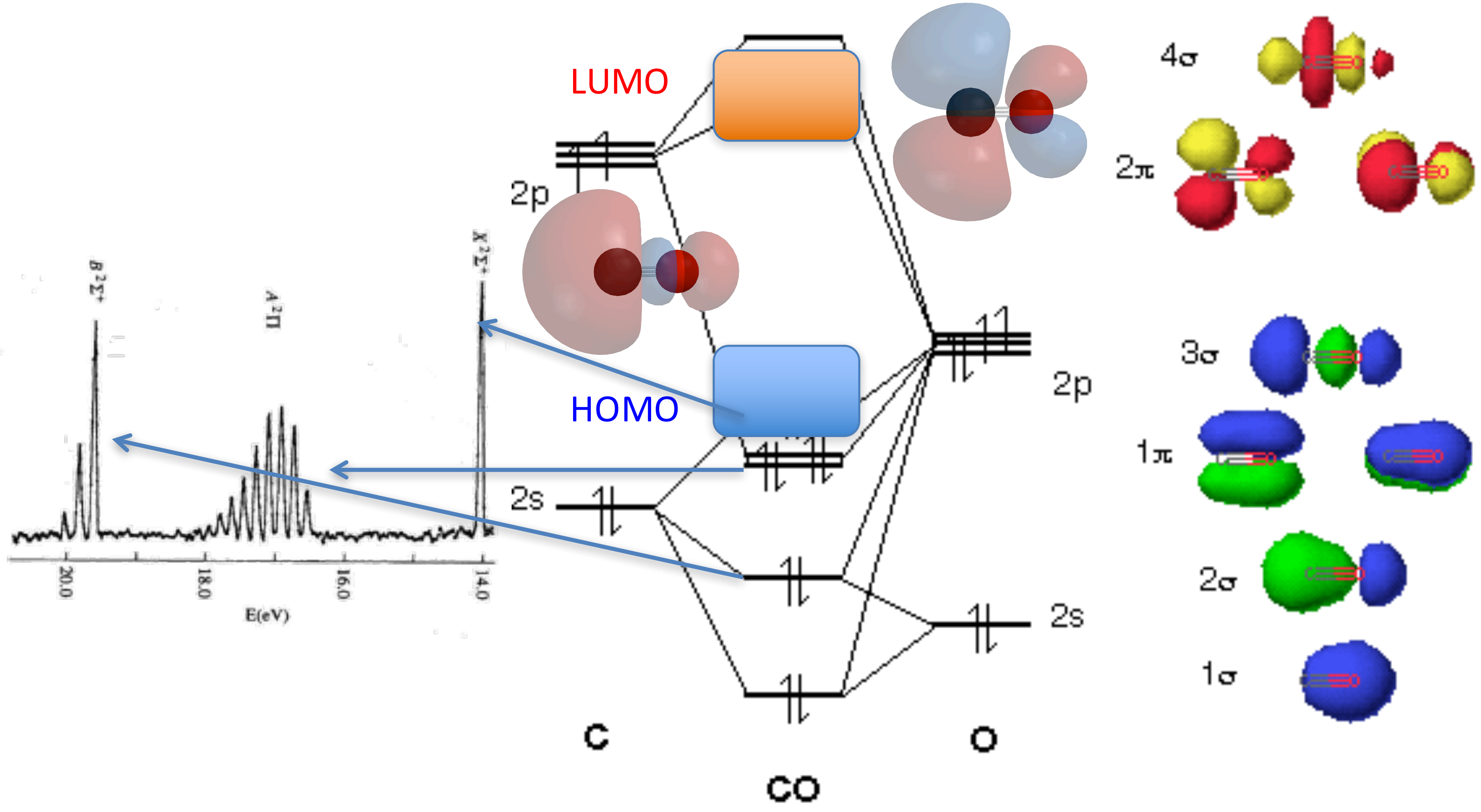
this orbital interaction responsible for designation
of these ligands as **π-acids**

Frontier MO's of π-Acceptor Ligands

This class of ligands donates e⁻s from a σ orbital
and these ligands accept e⁻s from the metal into an empty π* orbital.

CO is the archetype of this ligand class. Other π-acceptors are NO^+, CN^-, CNR.

the HOMO is filled and of σ-symmetry, the LUMO is empty and of π* symmetry



Electronic Structure and Properties of Complexes: Crystal Field Theory

Two theories are commonly used to rationalize electronic structure

- **Crystal Field Theory** (emerged from an analysis of the spectra of d-metal ions in the solid)
- **Ligand Field Theory** (emerged from an application of MO theory to d-metal complexes)

CFT Assumptions

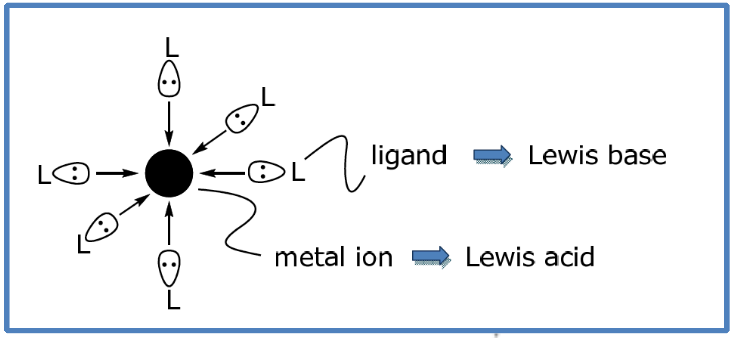
- Complexes held together via electrostatic forces between the positively charged metal and the negatively charged or polarized ligands

- Models interactions based on electrostatics with the valence electrons of the metal in the d-orbitals and the ligands as negative charges (ion-ion interactions) or dipoles (ion-dipole) interactions (**IONIC bonding model**)

- Stronger interactions between electrons of the metal and the ligands result in greater destabilization

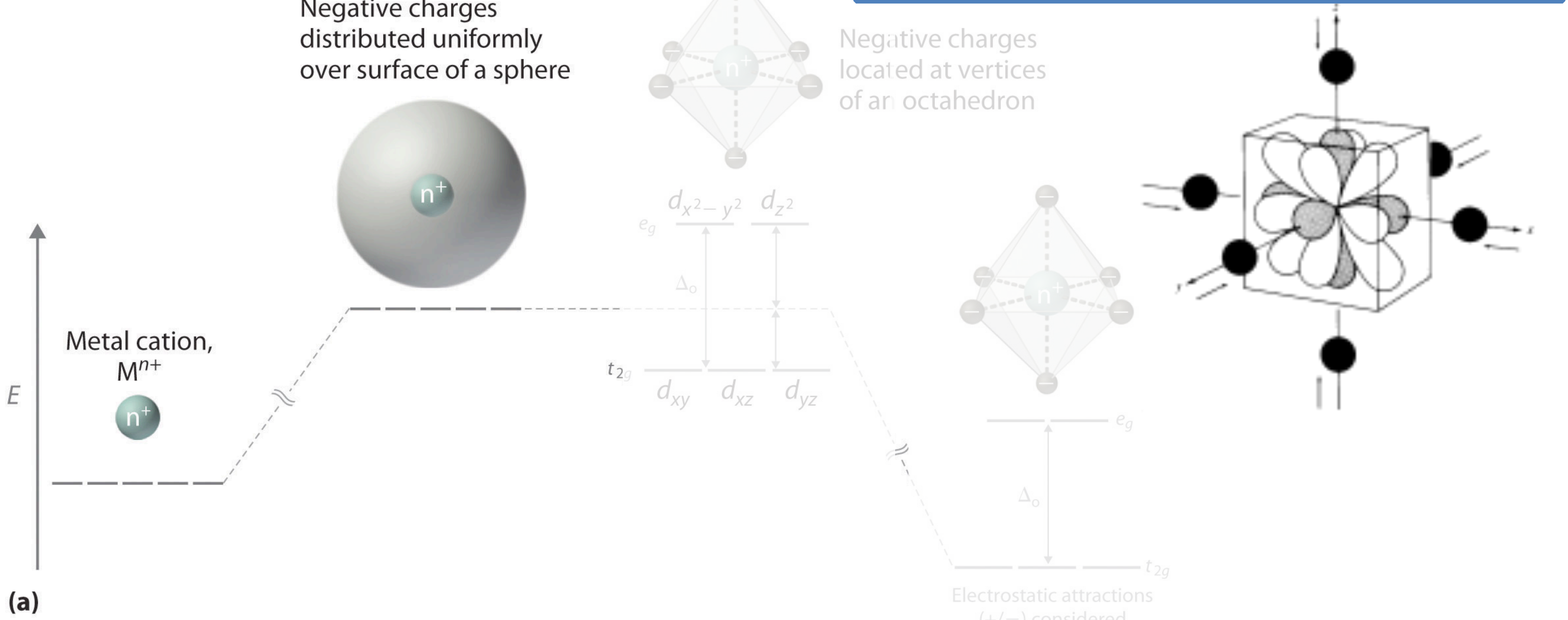
- The energy difference of d-orbitals correlates with the optical, magnetic and thermodynamic properties of the complex

Electronic Structure and Properties of Complexes: Crystal Field Theory



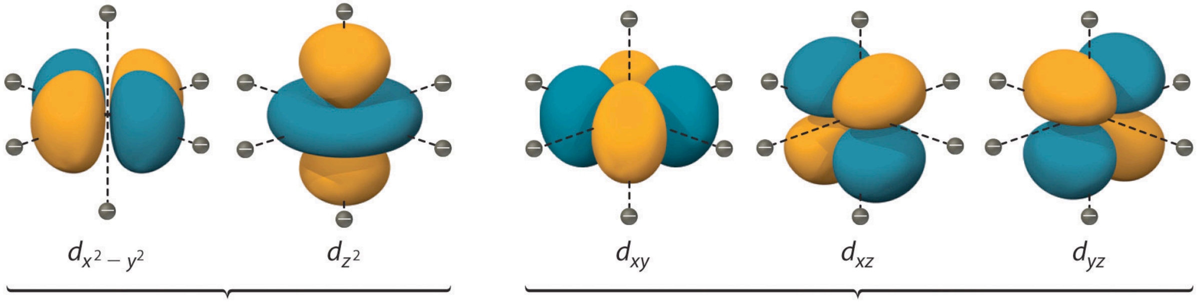
ligand ➡ Lewis base

metal ion ➡ Lewis acid



(a)

The lobes of the $d_{x2\text{-}y2}$ and d_{z2} orbitals lie directly along the x, y and/or z axes



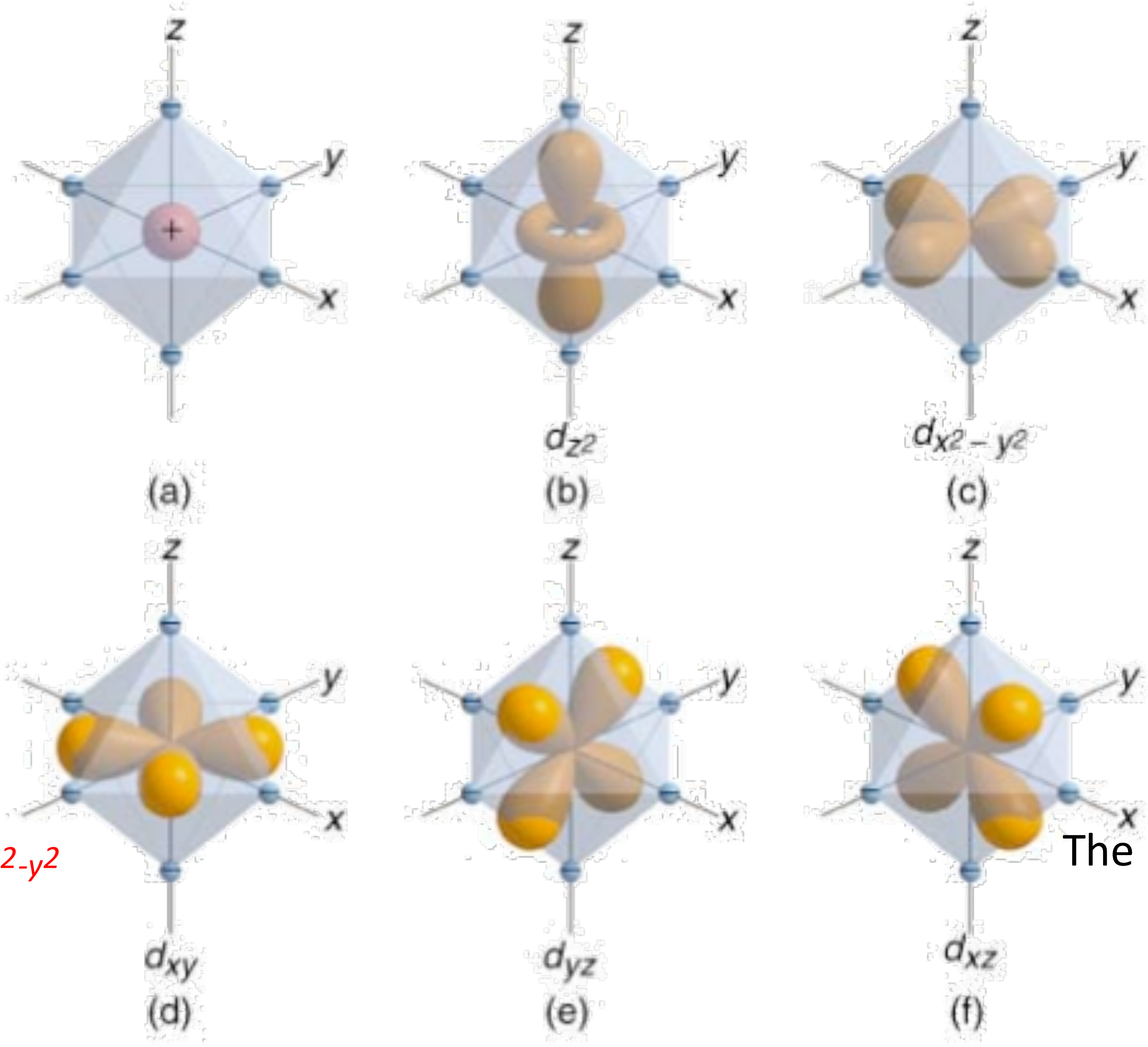
e_g orbitals go up in energy by $\frac{3}{5}\Delta_o$

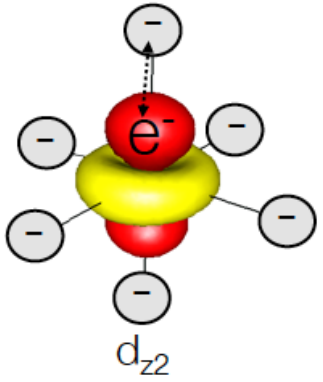
t_{2g} orbitals go down in energy by $\frac{2}{5}\Delta_o$

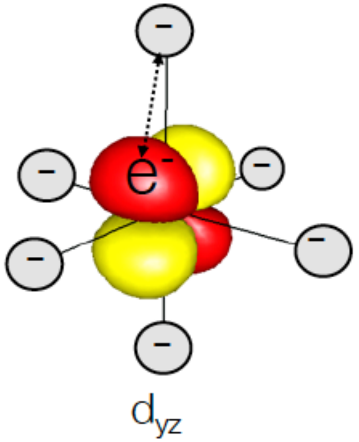
(b)

The lobes of the d_{xy}, d_{xz} and d_{yz} orbitals lie between the axes

Electronic Structure and Properties of Complexes: Crystal Field Theory



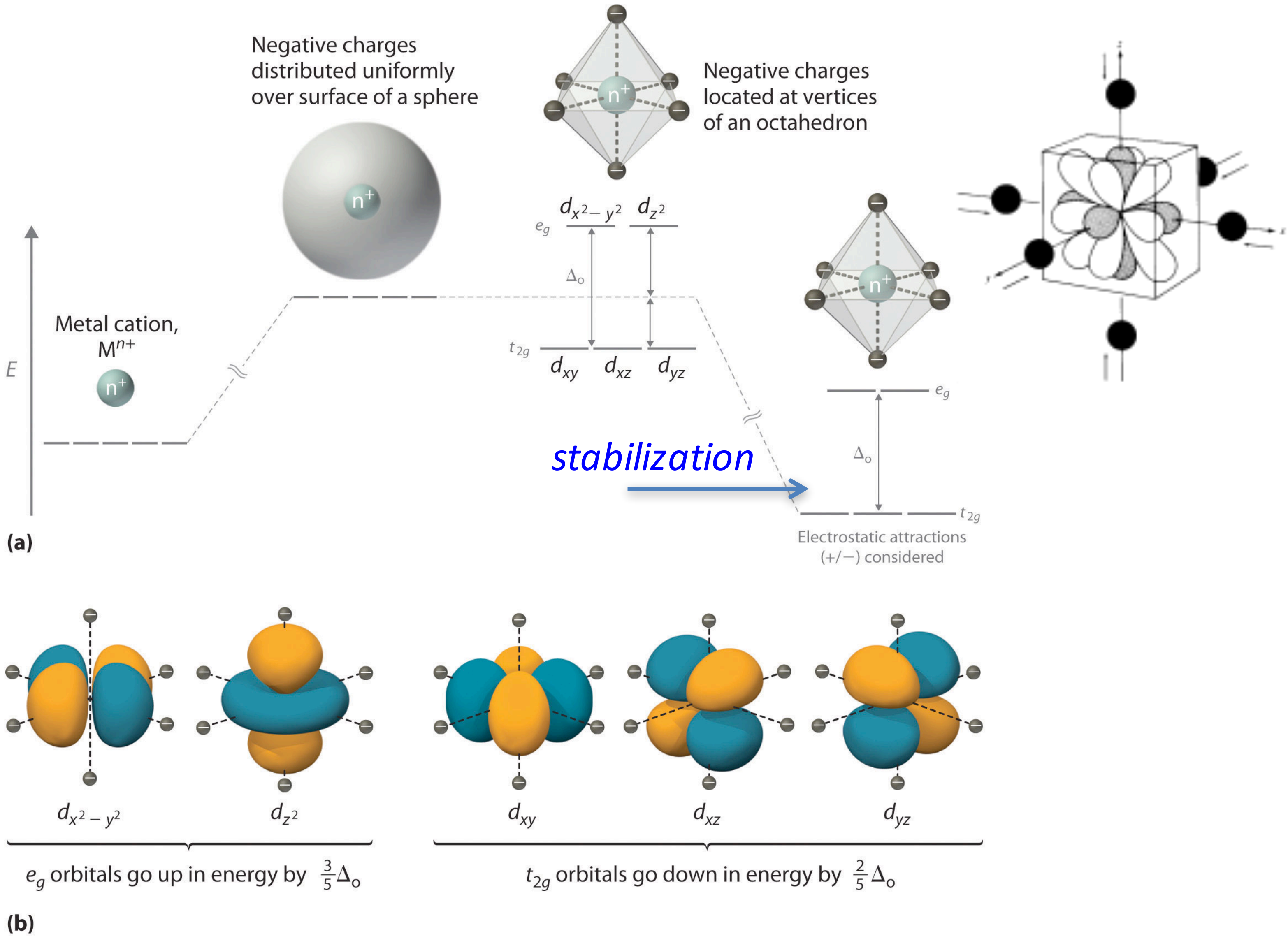




The lobes of the d_{x2-y2} and d_{z2} orbitals lie directly along the x, y and/or z axes

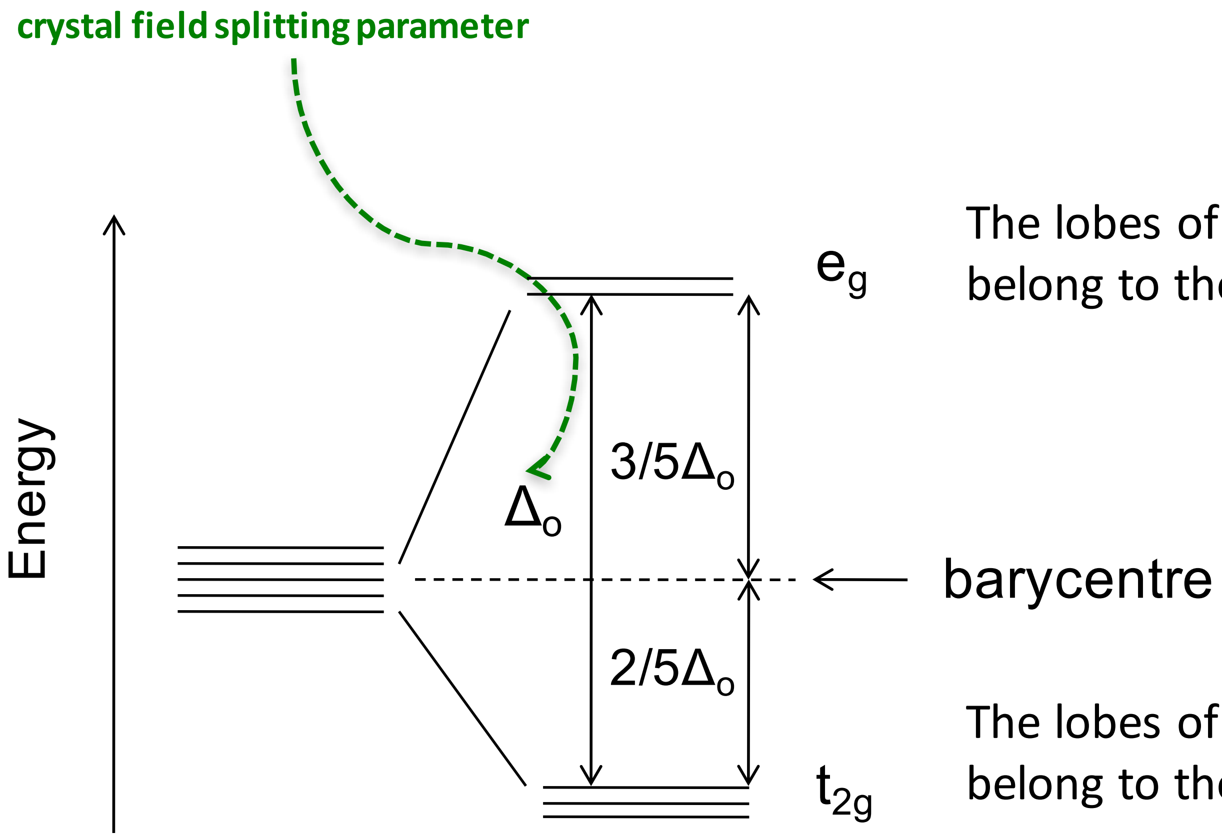
The lobes of the d_{xy}, d_{xz} and d_{yz} orbitals lie between the axes

Electronic Structure and Properties of Complexes: Crystal Field Theory



stabilization

Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex



The lobes of the $d_{x^2-y^2}$ and d_{z^2} belong to the e_g representation

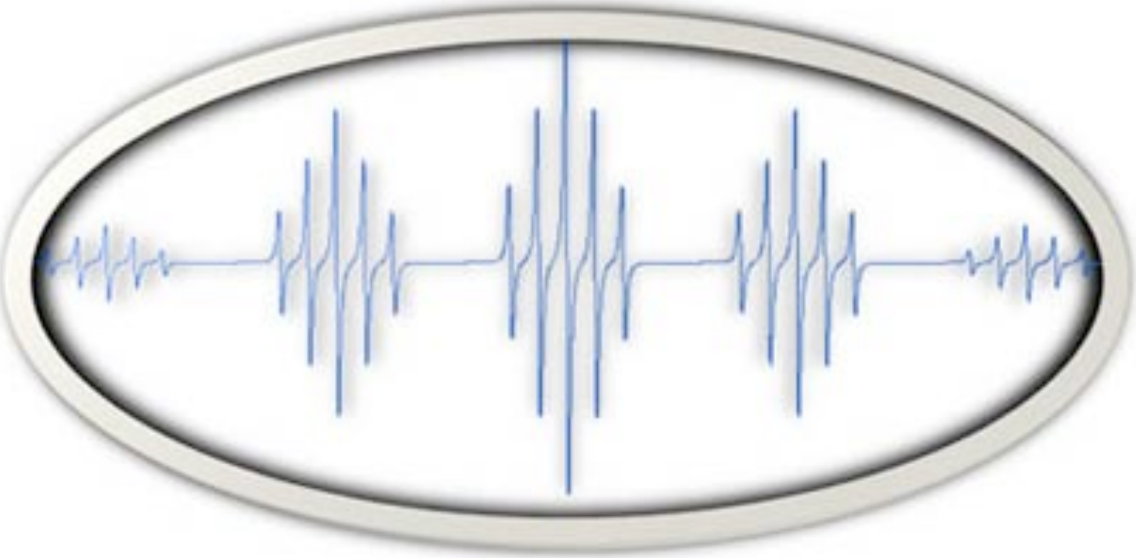
The lobes of the d_{xy}, d_{xz} and d_{yz} belong to the t_{2g} representation

- The energy difference between the two sets of orbitals is the **crystal field splitting energy** - denoted Δ_O (or $10D_q$)
- The e_g orbitals are raised in energy
- The t_{2g} orbitals are lowered in energy

Electronic Structure and Properties of Complexes: Crystal Field Theory Limitations & MO (LFT) Theory

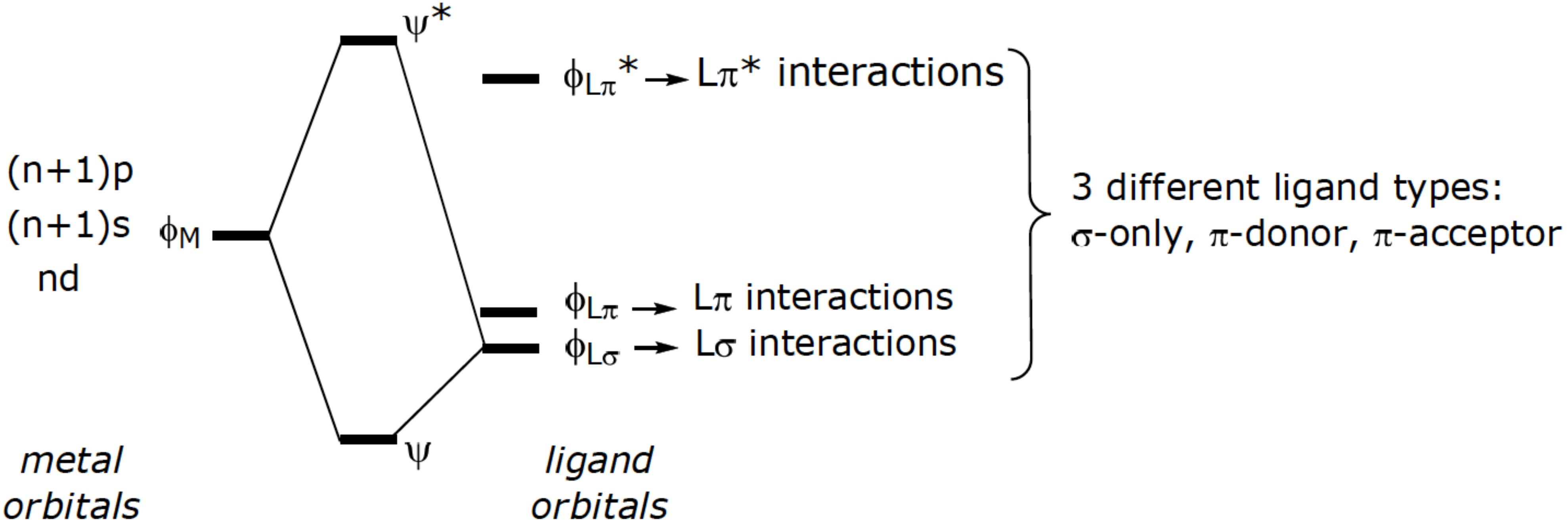
Questions for which Crystal Field Theory has no answers:

- Why is $KMnO_4$ with Mn^{7+} and no d-electrons coloured?
- Why is OH^- a weaker field ligand that H_2O?
- Why are neutral ligands like CO, which are otherwise very poor Lewis bases such strong field ligands?
- Why in EPR spectra of high spin complexes is there hyperfine splitting, indicating that the spin is delocalized onto the ligands?



MO (LFT) Theory

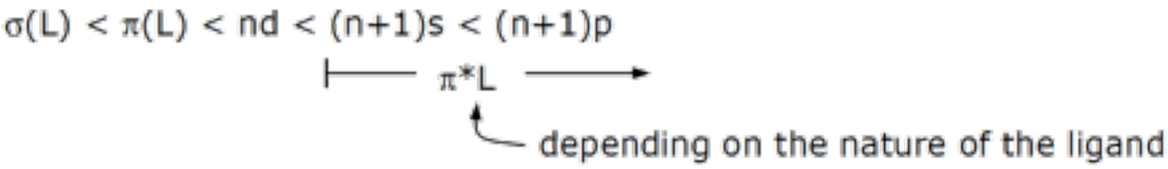
The interaction of the frontier atomic (for single atom ligands) or molecular (for many atom ligands) orbitals of the ligand and metal lead to bond formation



3 different ligand types: σ-only, π-donor, π-acceptor

Some important points:

- M—L atomic orbital mixing is proportional to the overlap of the metal and ligand orbital (S_{ML})
- Owing to more directional bonding (greater overlap) along the series $S_{ML}(\sigma) > S_{ML}(\pi) > S_{ML}(\delta)$, which leads to greater splitting along the series
- M–L atomic orbital mixing is inversely proportional to energy difference of mixing orbitals (i.e. ΔE_{ML})
- Only orbitals of correct symmetry can mix and the total MOs = sum of the precursor orbitals
- The order of the E_L and E_M energy levels almost always is:



$\sigma(L) < \pi(L) < nd < (n+1)s < (n+1)p$

$\pi^{*}L$

depending on the nature of the ligand

MO (LFT) Theory

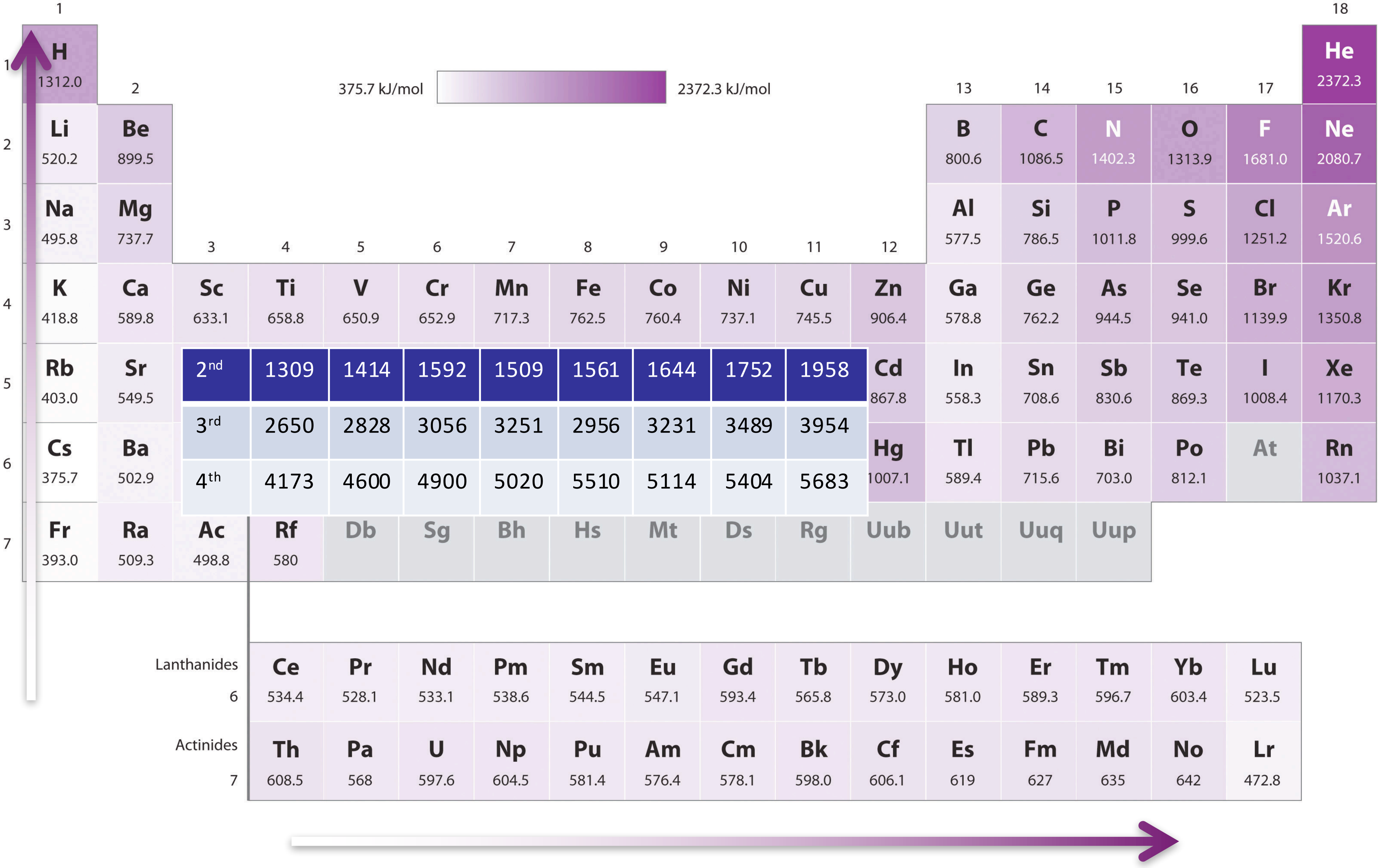
The interaction of the frontier atomic (for single atom ligands) or molecular (for many atom ligands) orbitals of the ligand and metal lead to bond formation

Some general observations:

- The s orbitals of L's are generally too low in energy to participate in bonding ($\Delta E_{ML}(\sigma)$ is very large)
- Filled p orbitals of L's are the frontier orbitals, and they have IEs that place them below the metal orbitals
- For molecular L's, whose frontier orbitals comprise s and p orbitals, here too filled ligand orbitals have energies that are stabilized relative to the metal orbitals
- Ligand orbital energy increases with decreasing E_{neg} of Lewis basic bonding atom $E(CH_3^-) > E(NH_2^-) > E(OH^-)$
- M orbital energy decreases with increase oxidation state of metal, as you go down the periodic table and as you go from left to right on the periodic table

MO (LFT) Theory

The interaction of the frontier atomic (for single atom ligands) or molecular (for many atom ligands) orbitals of the ligand and metal lead to bond formation



375.7 kJ/mol – 2372.3 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1312.0																	**He** 2372.3
2	**Li** 520.2	**Be** 899.5											**B** 800.6	**C** 1086.5	**N** 1402.3	**O** 1313.9	**F** 1681.0	**Ne** 2080.7
3	**Na** 495.8	**Mg** 737.7											**Al** 577.5	**Si** 786.5	**P** 1011.8	**S** 999.6	**Cl** 1251.2	**Ar** 1520.6
4	**K** 418.8	**Ca** 589.8	**Sc** 633.1	**Ti** 658.8	**V** 650.9	**Cr** 652.9	**Mn** 717.3	**Fe** 762.5	**Co** 760.4	**Ni** 737.1	**Cu** 745.5	**Zn** 906.4	**Ga** 578.8	**Ge** 762.2	**As** 944.5	**Se** 941.0	**Br** 1139.9	**Kr** 1350.8
5	**Rb** 403.0	**Sr** 549.5										**Cd** 867.8	**In** 558.3	**Sn** 708.6	**Sb** 830.6	**Te** 869.3	**I** 1008.4	**Xe** 1170.3
6	**Cs** 375.7	**Ba** 502.9										**Hg** 1007.1	**Tl** 589.4	**Pb** 715.6	**Bi** 703.0	**Po** 812.1	**At**	**Rn** 1037.1
7	**Fr** 393.0	**Ra** 509.3	**Ac** 498.8	**Rf** 580	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Uub**	**Uut**	**Uuq**	**Uup**			

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
2nd	1309	1414	1592	1509	1561	1644	1752	1958
3rd	2650	2828	3056	3251	2956	3231	3489	3954
4th	4173	4600	4900	5020	5510	5114	5404	5683

Lanthanides 6	**Ce** 534.4	**Pr** 528.1	**Nd** 533.1	**Pm** 538.6	**Sm** 544.5	**Eu** 547.1	**Gd** 593.4	**Tb** 565.8	**Dy** 573.0	**Ho** 581.0	**Er** 589.3	**Tm** 596.7	**Yb** 603.4	**Lu** 523.5
Actinides 7	**Th** 608.5	**Pa** 568	**U** 597.6	**Np** 604.5	**Pu** 581.4	**Am** 576.4	**Cm** 578.1	**Bk** 598.0	**Cf** 606.1	**Es** 619	**Fm** 627	**Md** 635	**No** 642	**Lr** 472.8

Electronic Structure and Properties of Complexes: LFT Theory

What is Ligand Field Theory?

It is:

- A **semi-empirical theory** that applies to a *class of substances* (transition metal complexes)
- A **language** in which a vast number of experimental observations can be rationalized and discussed
- A **model** that applies only to a restricted part of reality

It is not:

- An ***ab initio* theory** that lets one predict the properties of a compound
- A physically rigorous treatment of the electronic structure of transition metal complexes

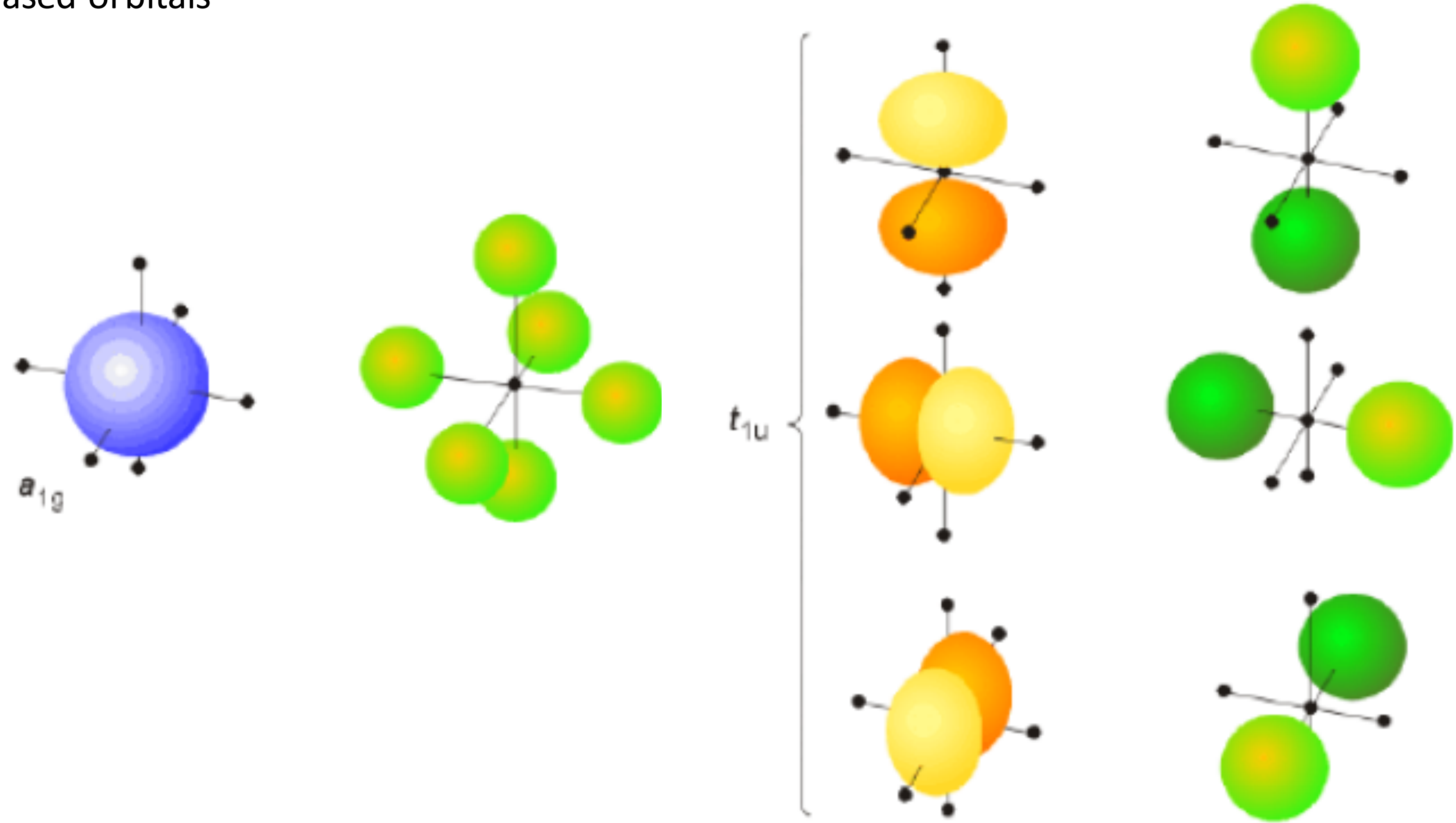
Electronic Structure and Properties of Complexes: LFT Theory

Sigma (σ) bonding

- Neutral ligands (e.g., NH_3) or anionic ligands (e.g., F^-) possess lone pairs that can bond to metal-based orbitals (s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{x2-y2}, d_{z2}) with σ-symmetry
- In an O_h complex, 6 symmetry-adapted linear combinations (SALCs) of the 6 ligand σ-symmetry orbitals can be formed
- MOs for the resulting complex are formed by combining the ligand SALCs and the metal-based d-orbitals of the same symmetry type
- With 6 SALCs combined with the metal MOs, we will get 6 bonding and 6 antibonding MOs – now called **ligand group orbitals (LGOs)**
- The resulting MO diagram now gets populated with the electrons according to the Aufbau process, Pauli exclusion principle and Hund's rule

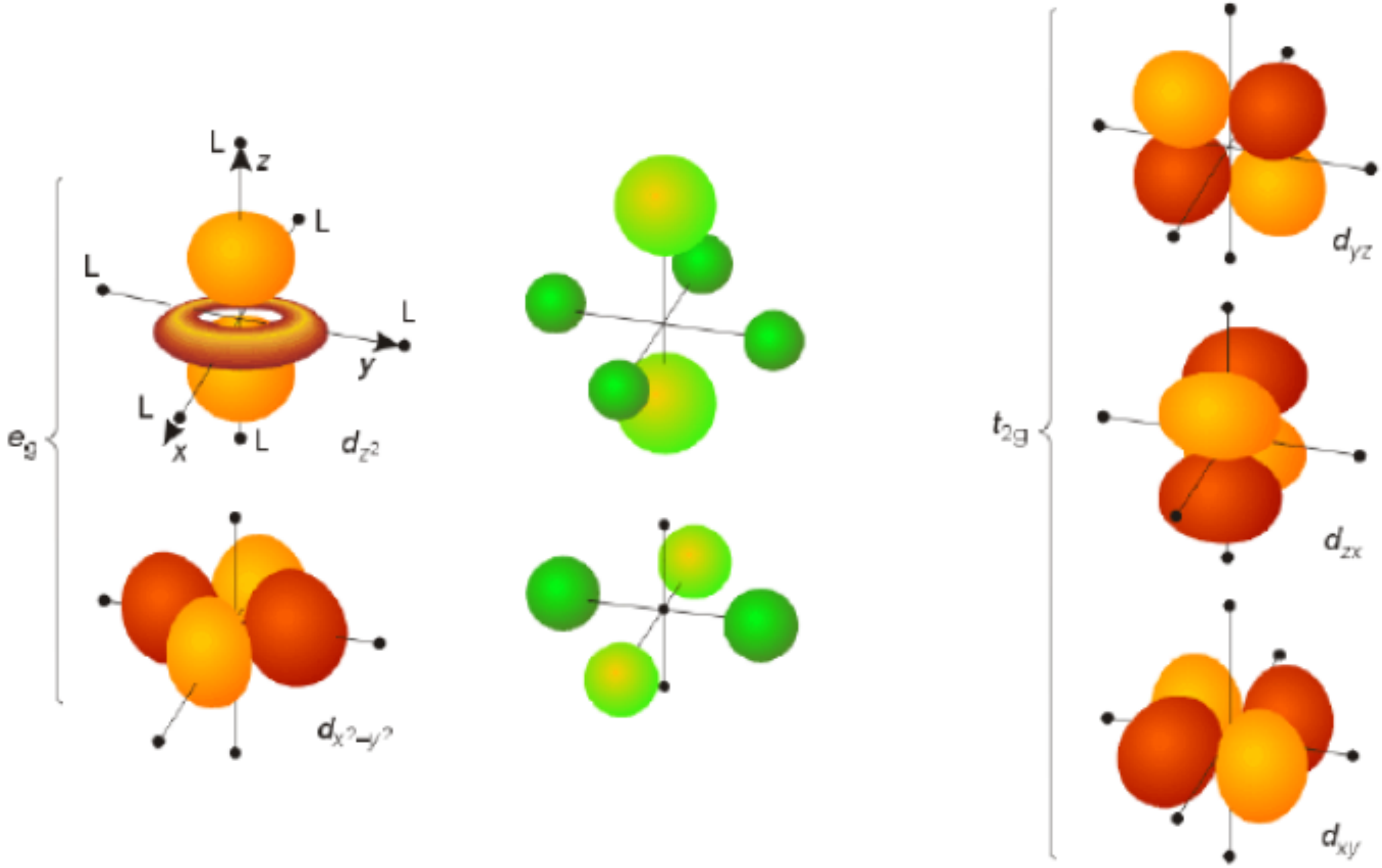
Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Sigma (σ) bonding: Simple example showing interaction of ligand s-orbitals with metal-based orbitals



Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Sigma (σ) bonding: Simple example showing interaction of ligand s-orbitals with metal-based orbitals

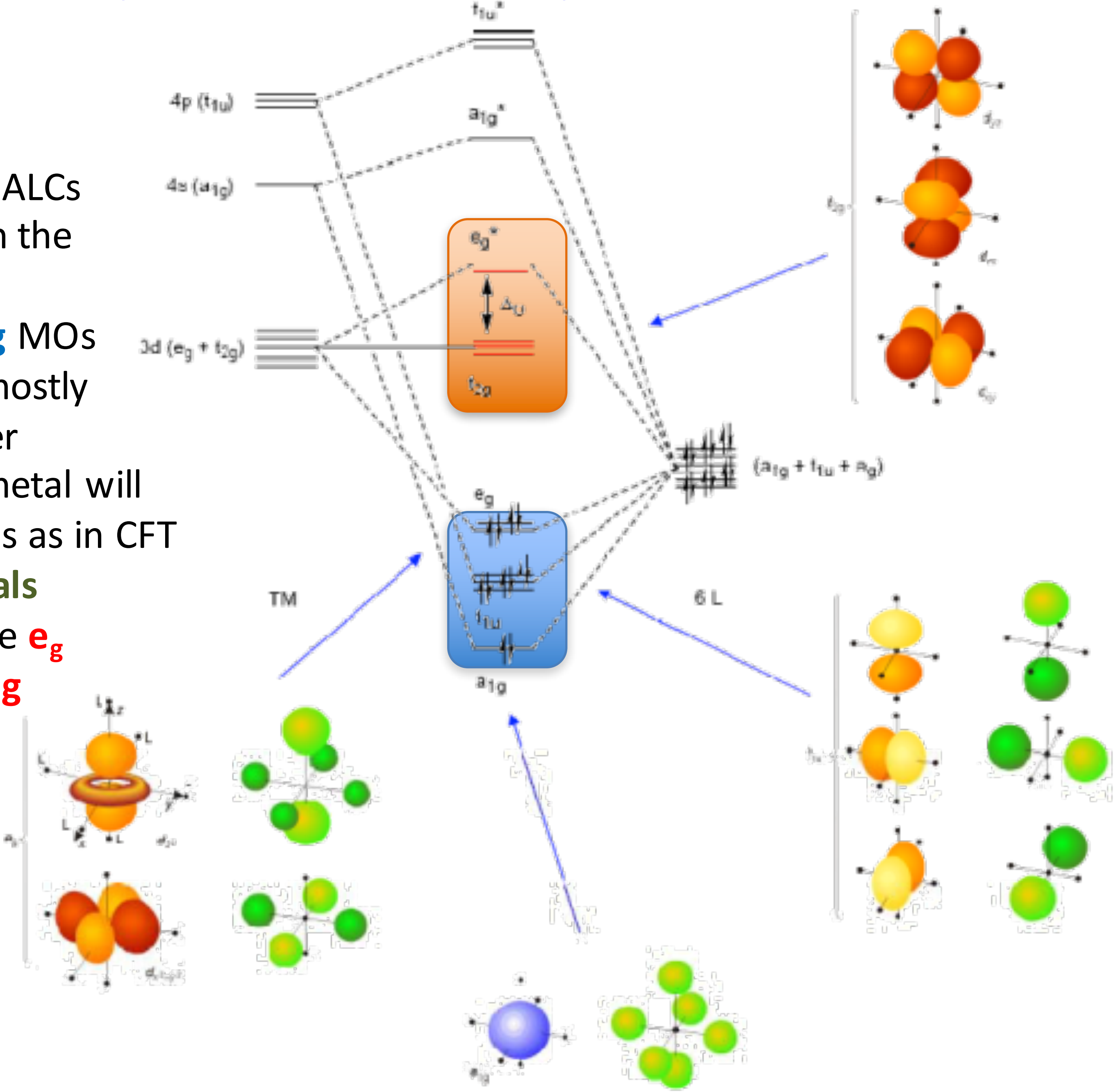


not proper symmetry so no interaction

Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Sigma (σ) bonding:

- For most ligands, their SALCs are lower in energy than the metal-based d-orbitals
- Therefore the 6 **bonding** MOs of the complex will be mostly ligand-based in character
- The d-electrons of the metal will occupy the ***same*** orbitals as in CFT
- Unlike CFT, the **t_{2g} orbitals are non-bonding** and the **e_g orbitals are anti-bonding**



Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

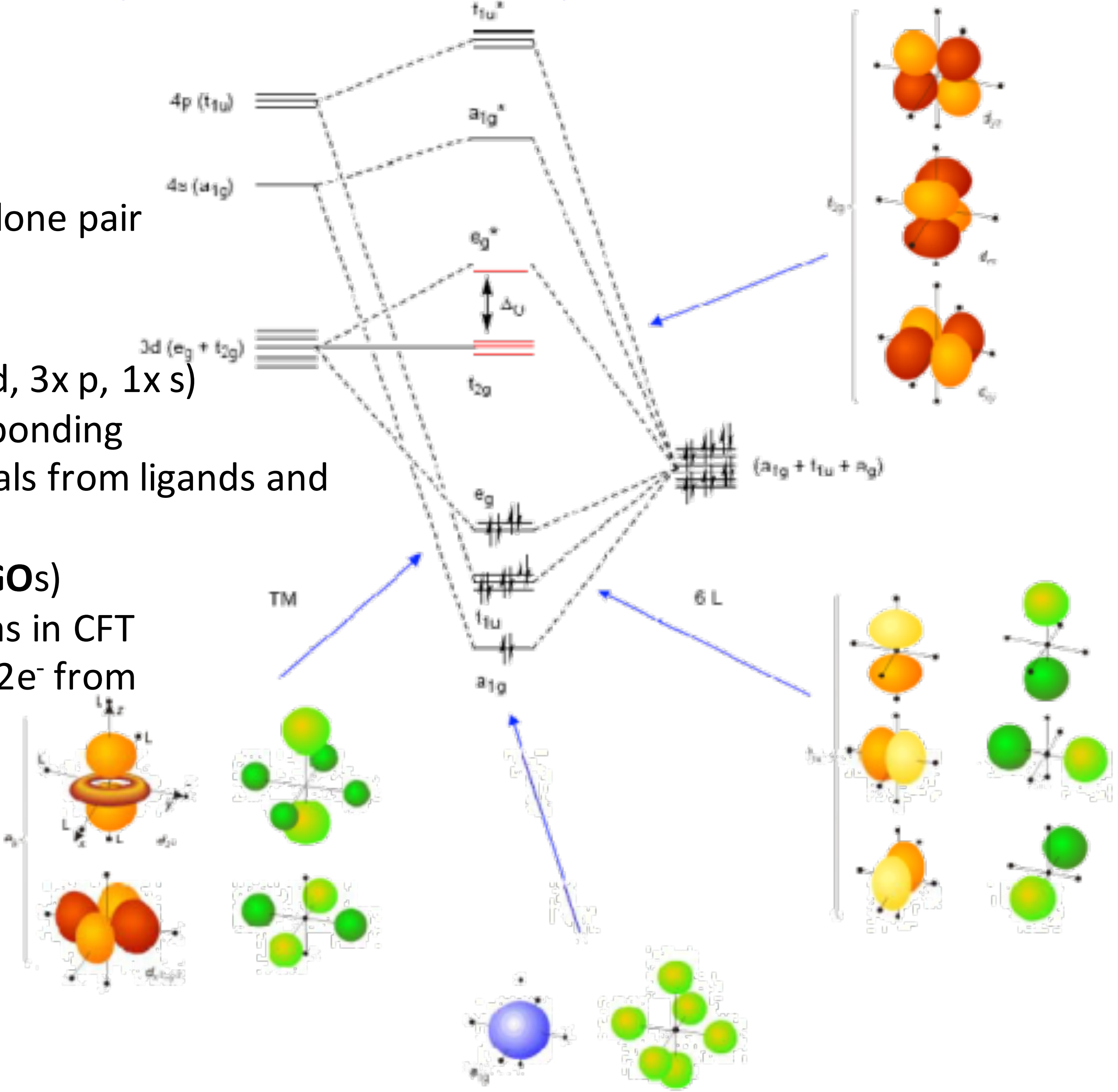
Example

Take $[Co(NH_3)_6]^{3+}$

NH_3 can σ-bond through its lone pair

To summarize:

- Of 9 valence orbitals (5x d, 3x p, 1x s) only 6 are suitable for σ-bonding
- The combination of orbitals from ligands and from metal are called **L**igand **G**roup **O**rbitals (**LGO**s)
- The Δ_O here is the same as in CFT
- Co^{3+} is d^6 and there are $12e^-$ from the 6 NH_3 ligands
- As this is a diamagnetic LS complex, the 6-d electrons occupy only the t_{2g} set

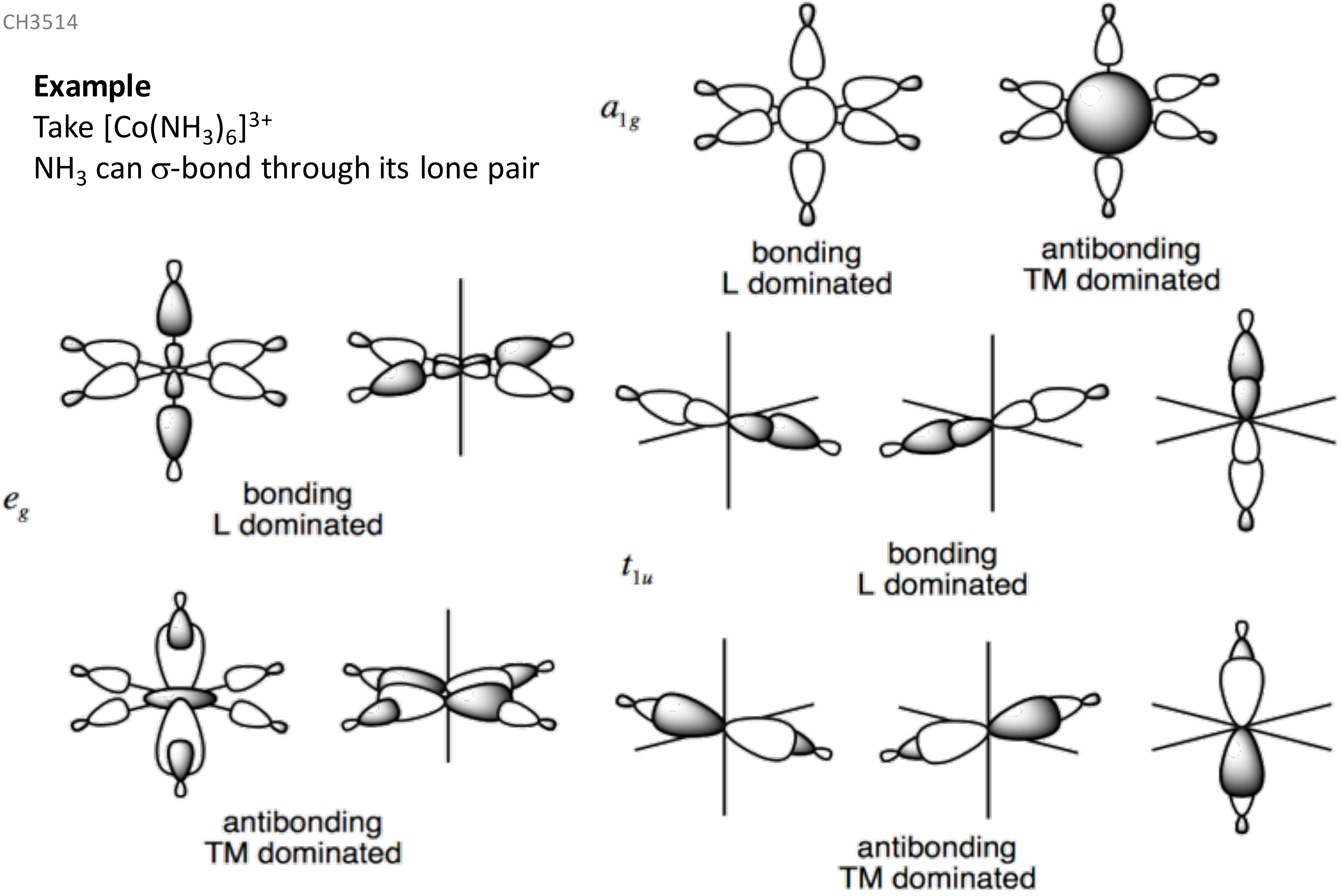


Electronic Structure and Properties of Complexes:
LFT Theory – Octahedral Complexes

Example

Take $[Co(NH_3)_6]^{3+}$

NH_3 can σ-bond through its lone pair

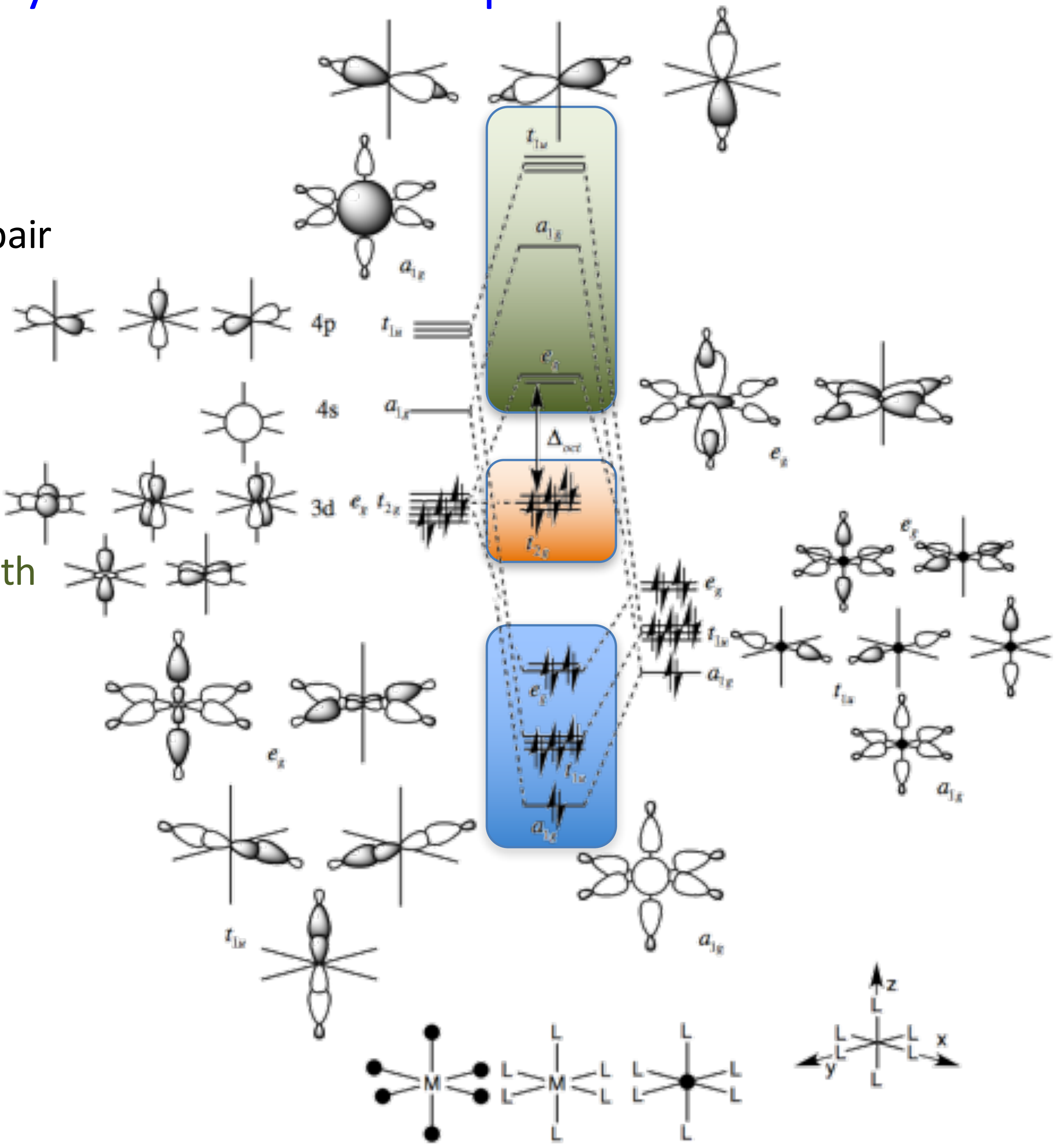


Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Example

Take $[Co(NH_3)_6]^{3+}$

NH_3 can σ-bond through its lone pair



ligand-based bonding MOs with strong ligand contributions

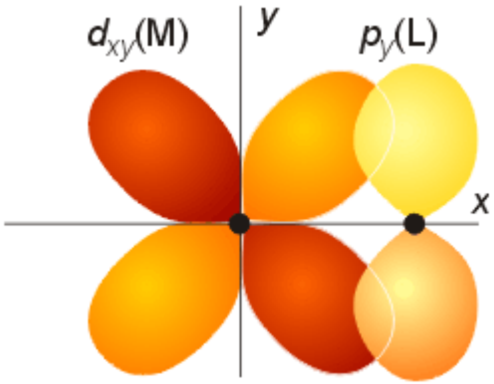
metal-based non-bonding AOs

metal-based anti-bonding MOs with strong metal AO contributions

Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

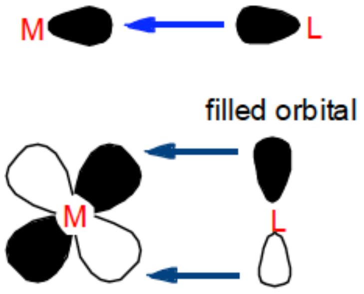
Pi (π) bonding:

- The previous MO diagram ignores π bonding. If the ligands possess orbitals of local π-symmetry then these can interact with the metal d-orbitals with the same symmetry (i.e. the t_{2g} set) to form new LGOs
- These ligand SALCs can act as electron donors (populated) or electron acceptors (vacant)



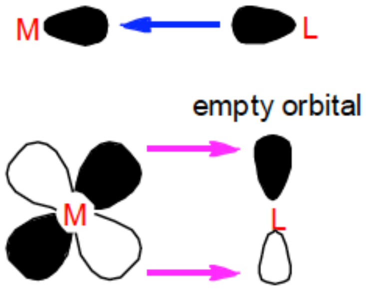
σ-donor

NH_3, CH_3^-, H^-



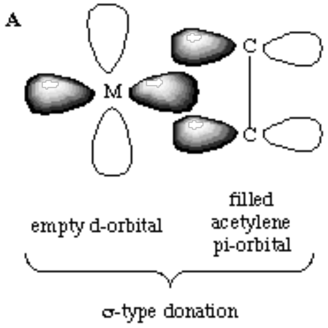
π-donor

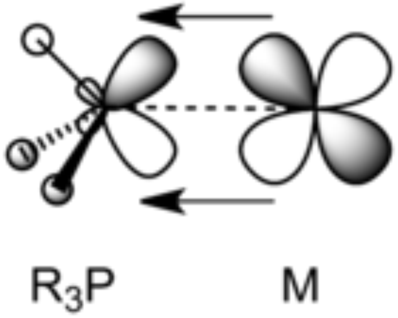
Cl^-, OH^-, NR_2^-, OH_2

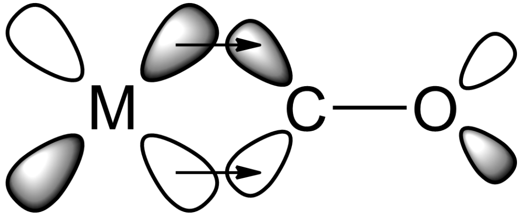


π-acceptor

CO, NO^+, CN^-



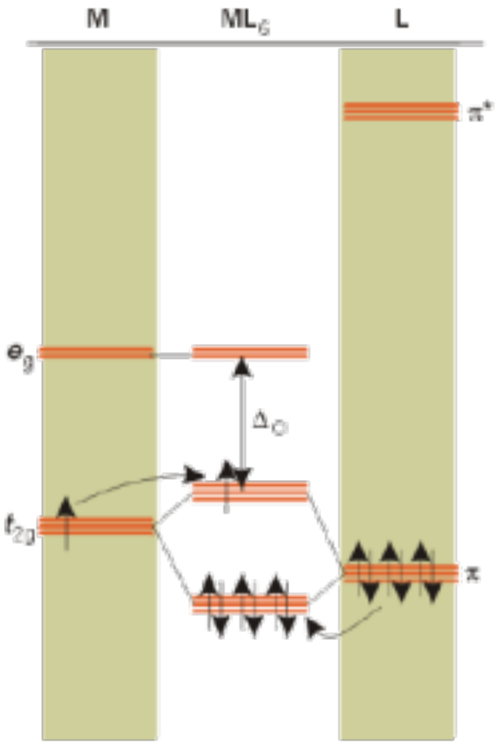




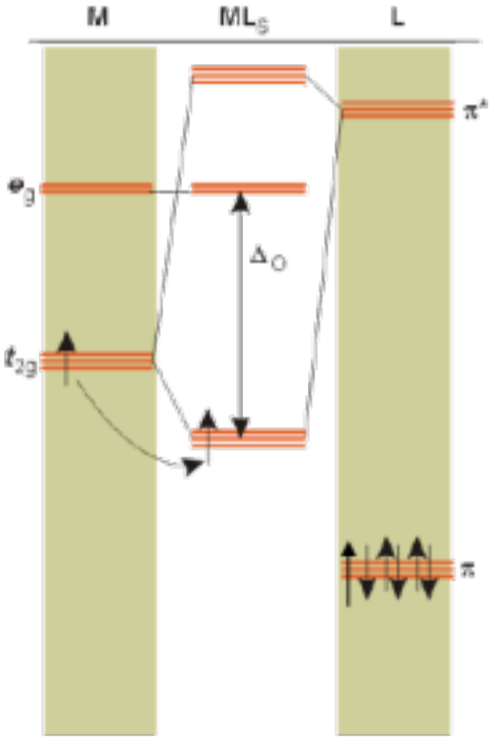
Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) bonding:

- The previous MO diagram ignores π bonding. If the ligands possess orbitals of local π-symmetry then these can interact with the metal d-orbitals with the same symmetry (i.e. the t_{2g} set) to form new LGOs
- These ligand SALCs can act as electron donors (populated) or electron acceptors (vacant)
- The nature of this secondary interaction will affect Δ_o



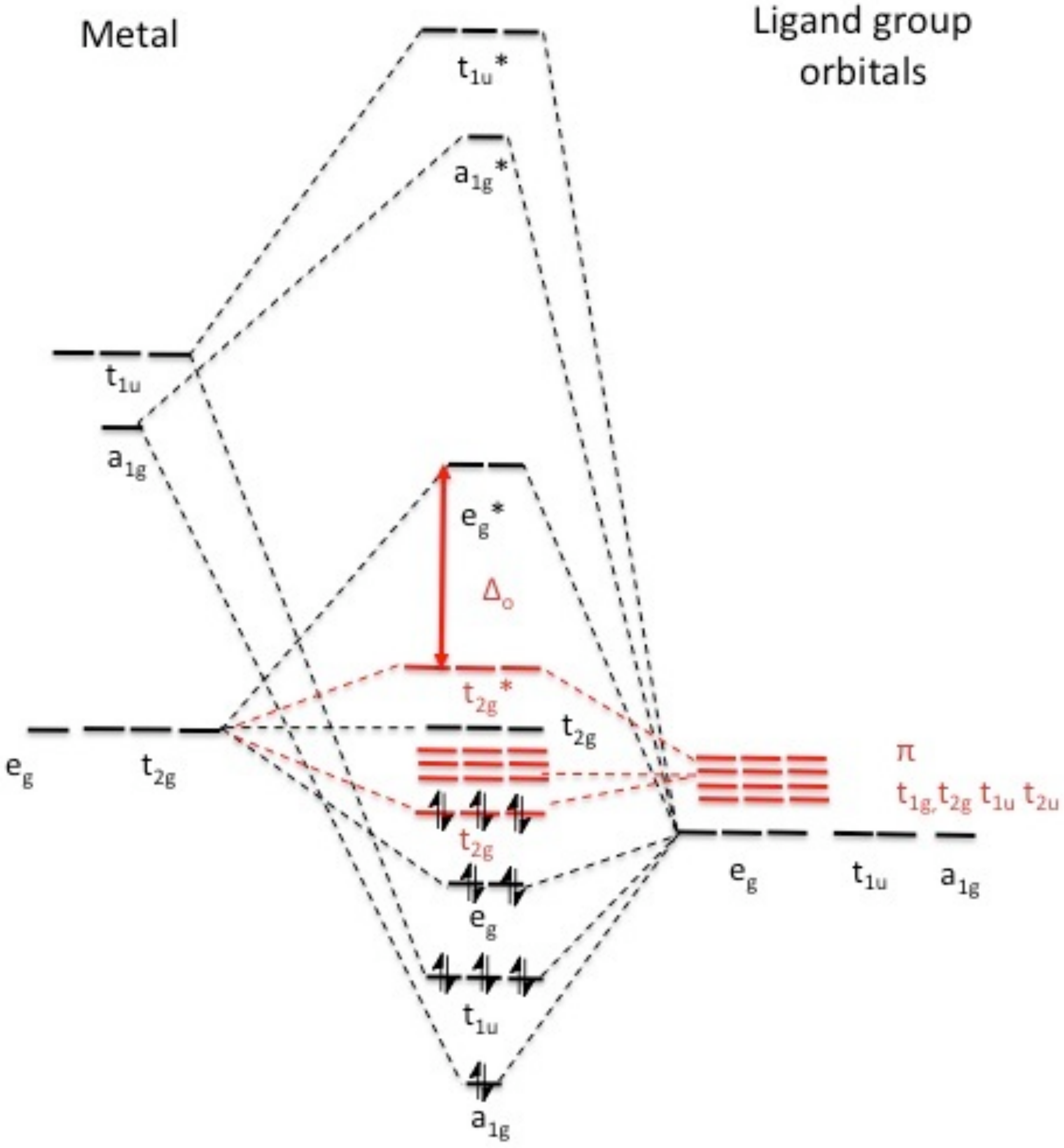
Ligands that are π donors decrease Δ_o.



Ligands that are π acceptors increase Δ_o.

Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) donor ligands:
(aka π-bases)

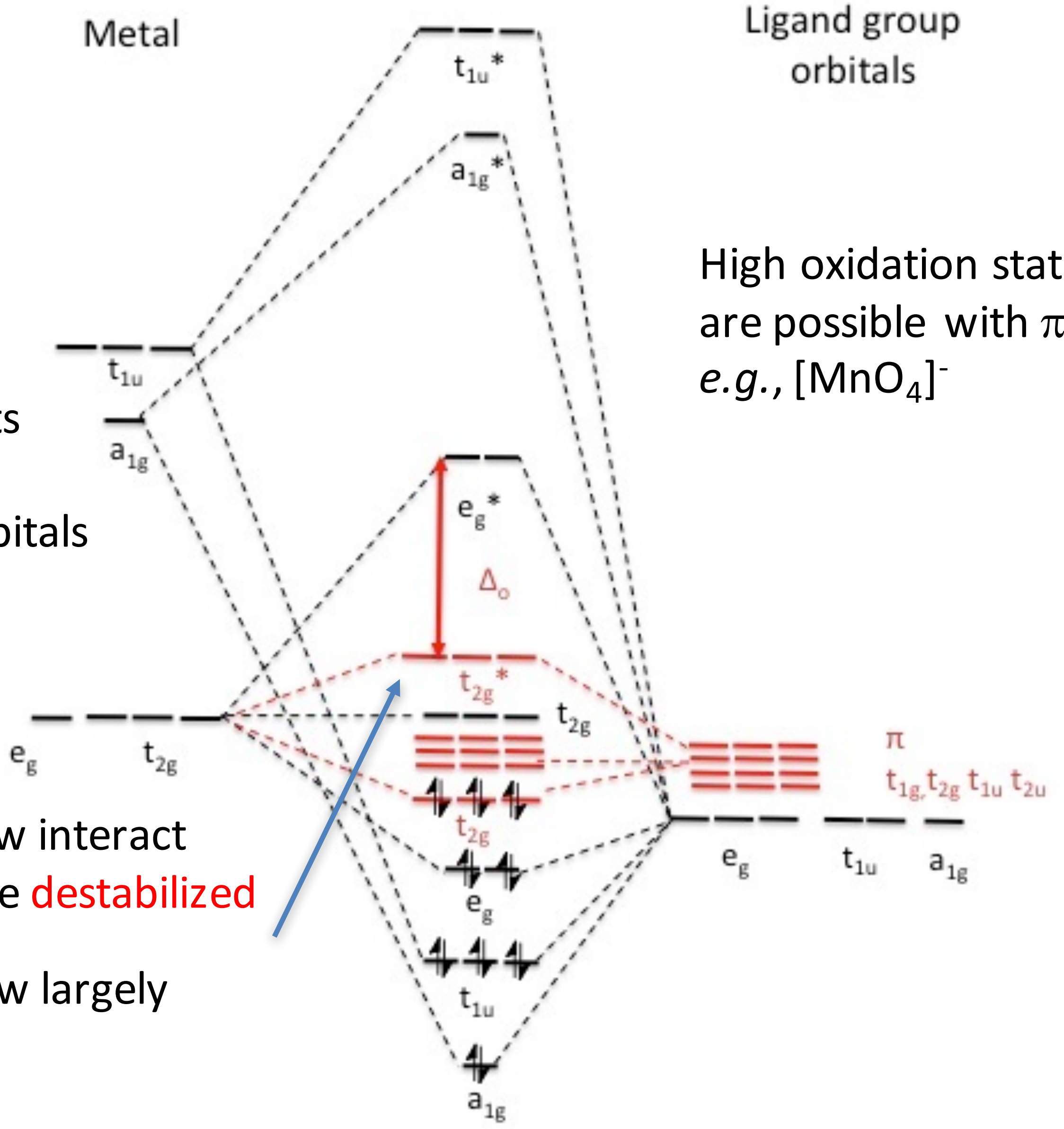


Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) donor ligands:
(aka π-bases)

Example
Take $[FeCl_6]^{3-}$

Cl can σ-bond through its lone pair AND π-bond through its p-orbitals



High oxidation state complexes are possible with π-base ligands *e.g.*, $[MnO_4]^-$

The Cl^- p orbitals can now interact with the Fe t_{2g}, which are destabilized

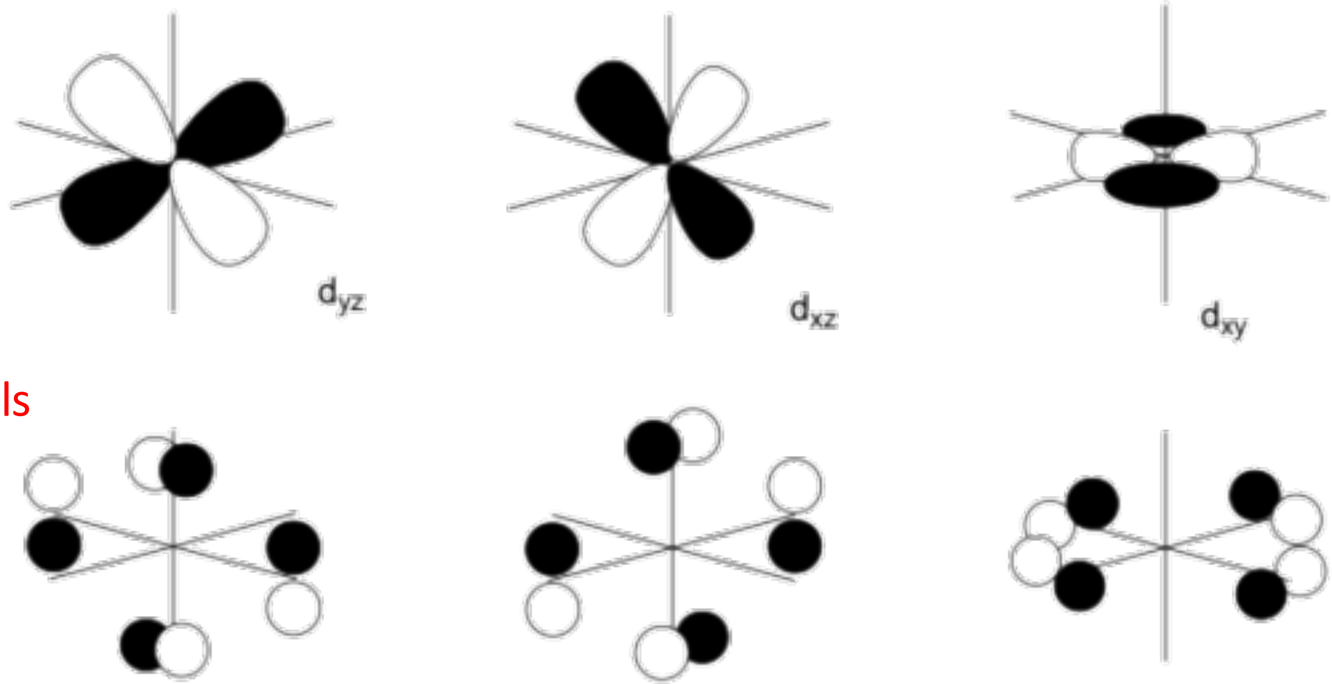
These complexes are now largely high spin

Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) donor ligands:
(aka π-bases)

Example
Take $[FeCl_6]^{3-}$

Cl can σ-bond through its lone pair AND
π-bond through its p-orbitals



The Cl^- p orbitals can now interact with the Fe t_{2g}, which are destabilized

These complexes are now largely high spin

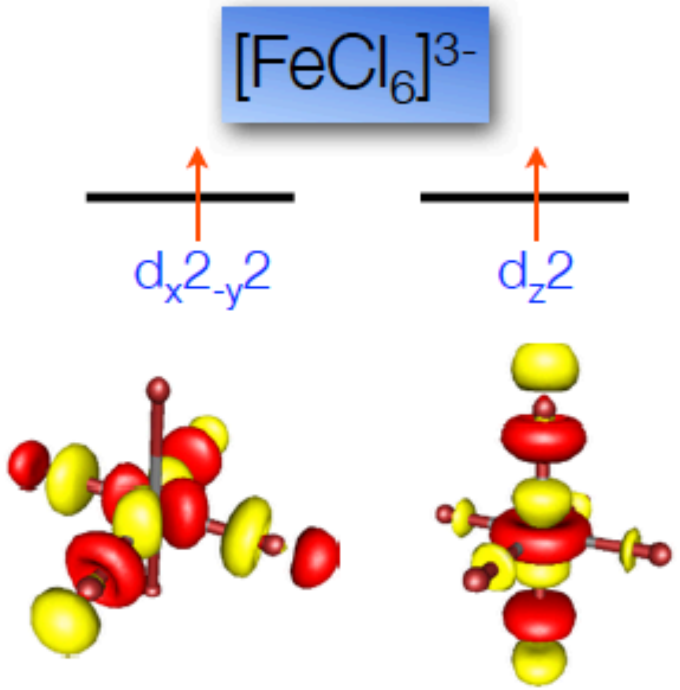
Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) donor ligands:
(aka π-bases)

Example
Take $[FeCl_6]^{3-}$

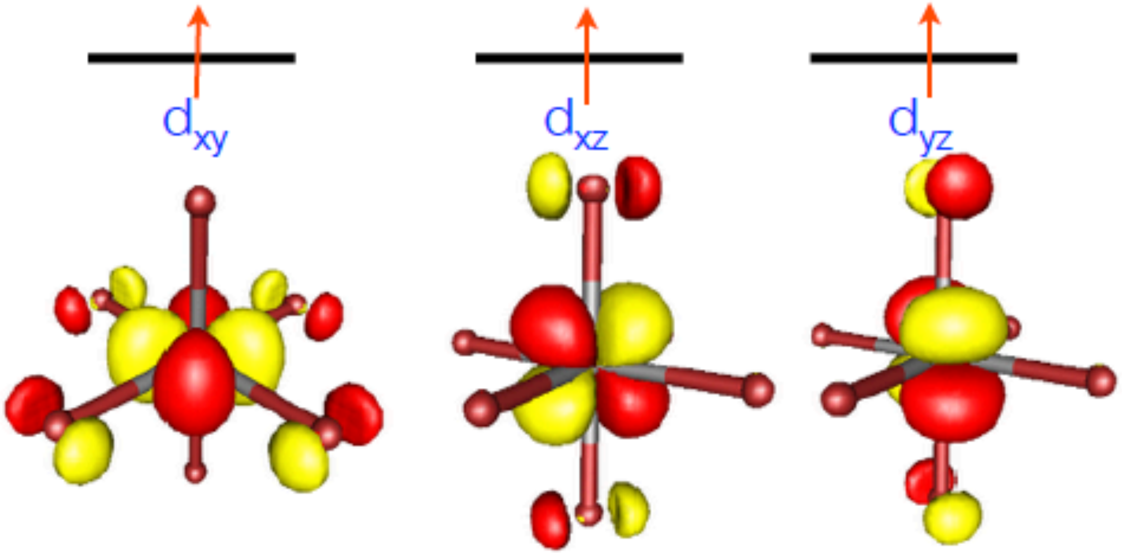
Cl can σ-bond through its
lone pair AND
π-bond through its p-orbitals

Both Fe-centered
t_{2g} and e_g
are antibonding!



The Cl^- p orbitals can now interact with the Fe t_{2g}, which are destabilized

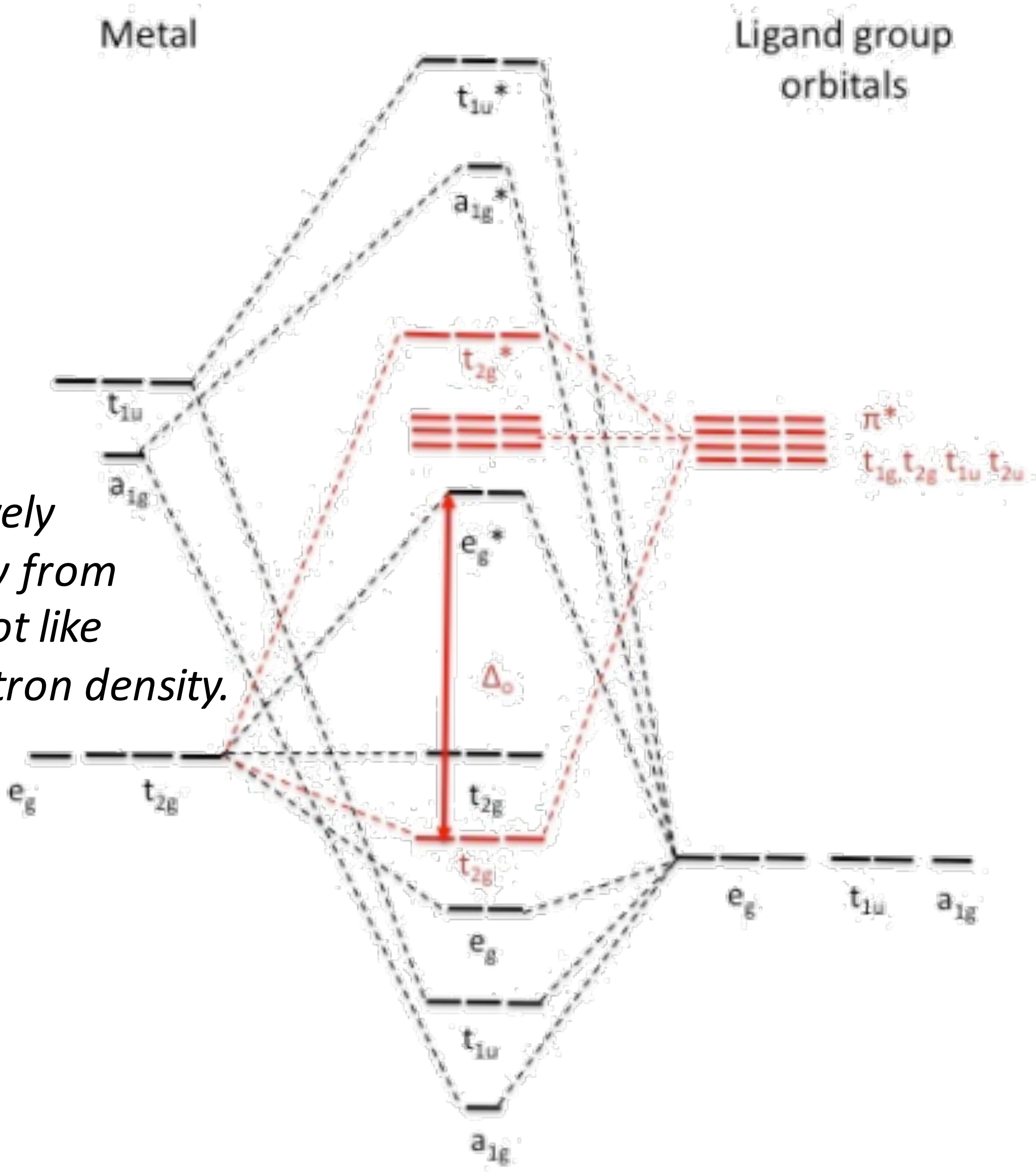
These complexes are now largely high spin



Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) acceptor ligands:
(aka π-acids)

π-backbonding effectively removes electron density from the metal, which does not like to have too high an electron density.

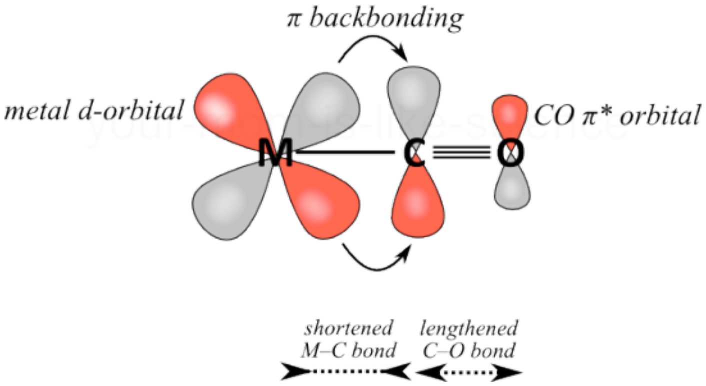


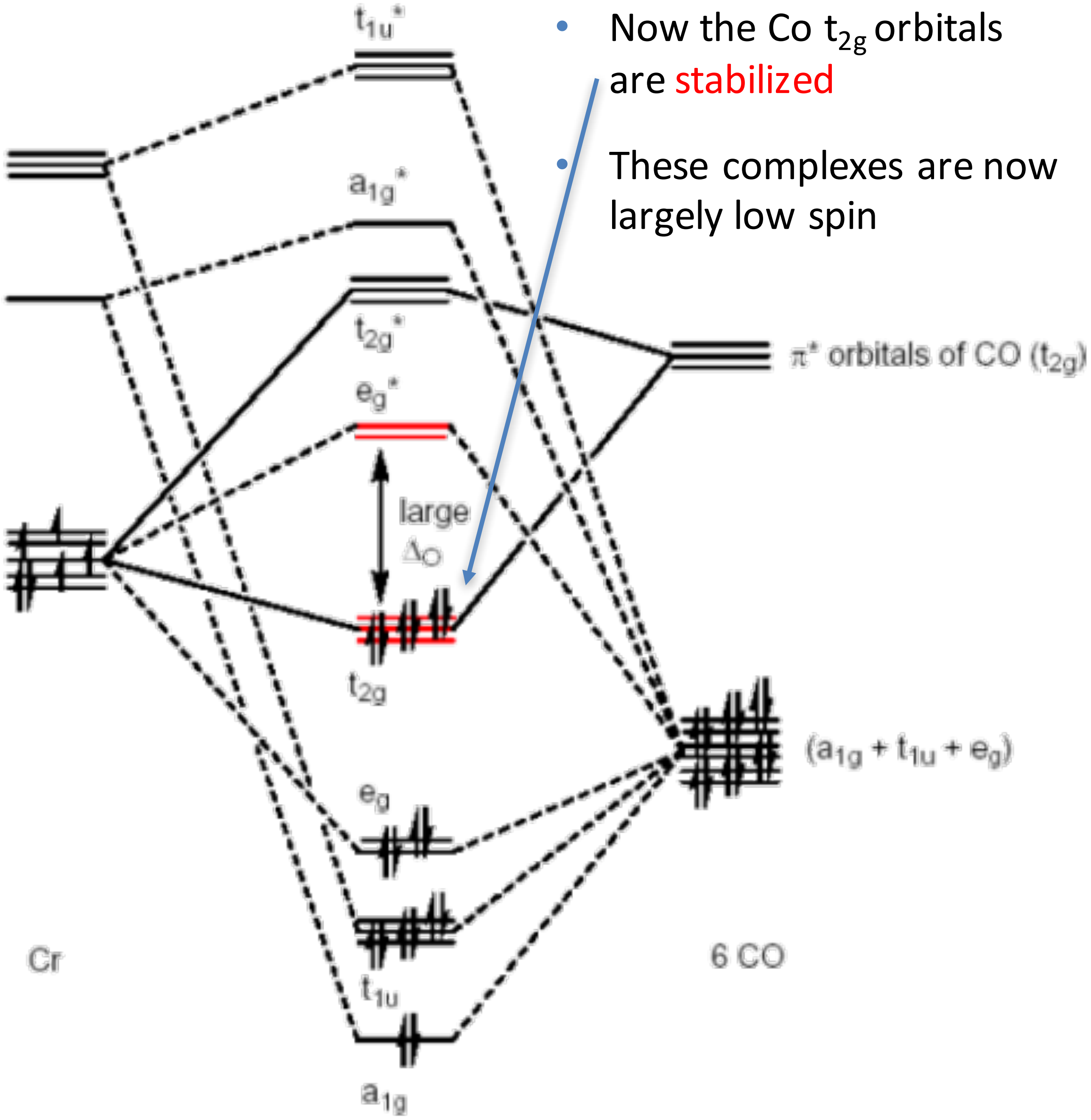
Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) acceptor ligands:
(aka π-acids)

Example
Take [$Cr(CO)_6$]

CO can σ-bond through its lone pair on C AND
π-bond through its p-orbitals
AND
its π* orbitals can form bonding interactions with metal d orbitals





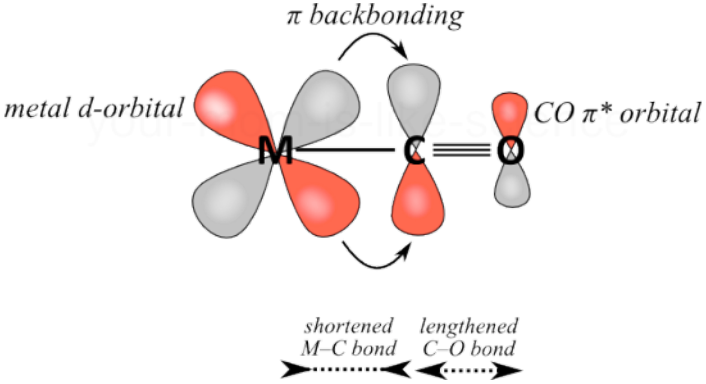
- Now the Co t_{2g} orbitals are stabilized
- These complexes are now largely low spin

Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

Pi (π) acceptor ligands:
(aka π-acids)

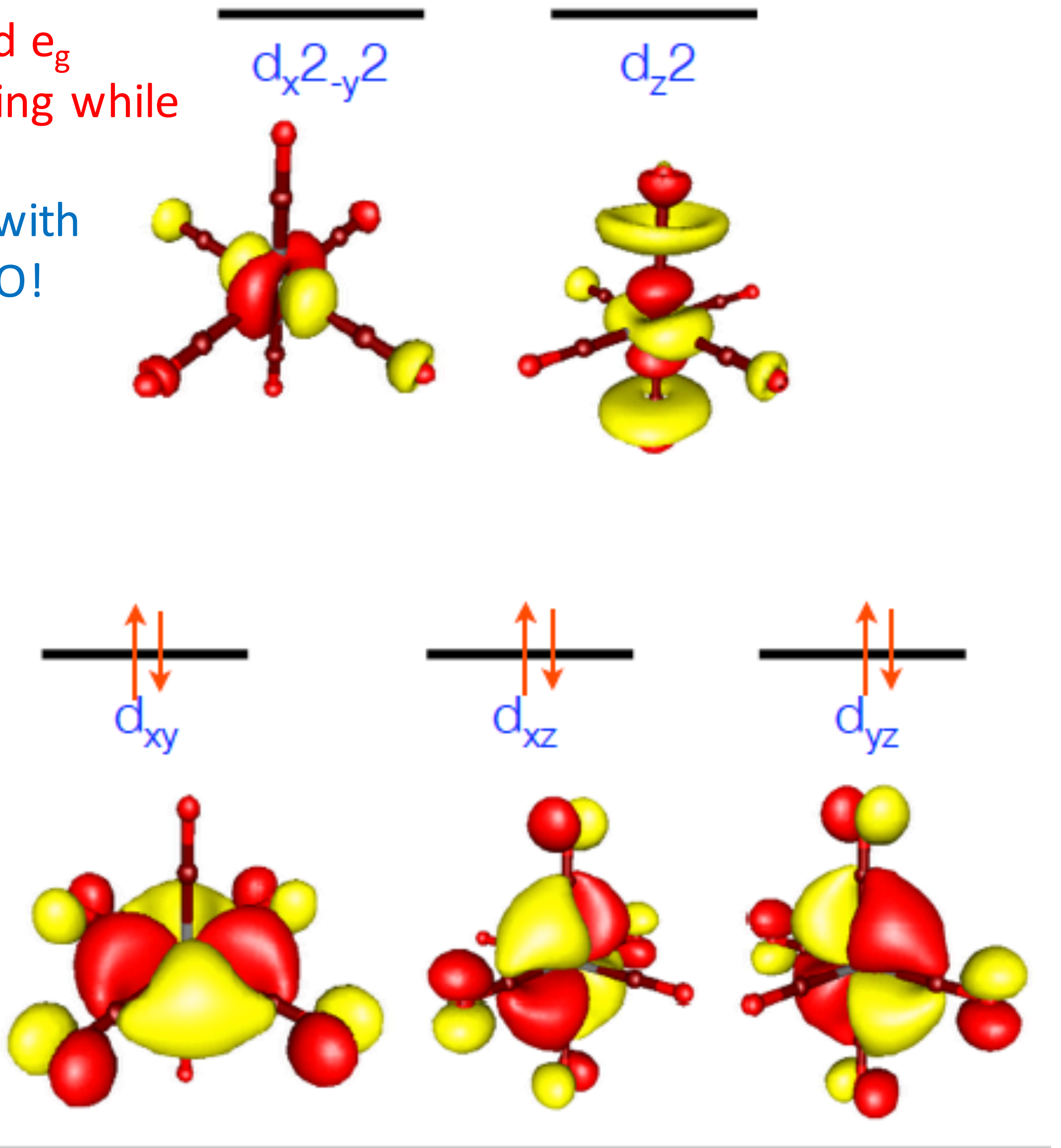
Example
Take $[Cr(CO)_6]$

CO can σ-bond through its lone pair on C AND
π-bond through its p-orbitals
AND
its π* orbitals can form bonding interactions with metal d orbitals



$[Cr(CO)_6]$

Co-centered e_g is antibonding while
t_{2g} is bonding with the π* of CO!



Electronic Structure and Properties of Complexes: Crystal Field Theory Limitations & MO (LFT) Theory

Summary: π-bonding and π-back bonding modulate the energy of the metal t_{2g} orbitals

$I^- < S^{2-} < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO \sim NO < NO^+$

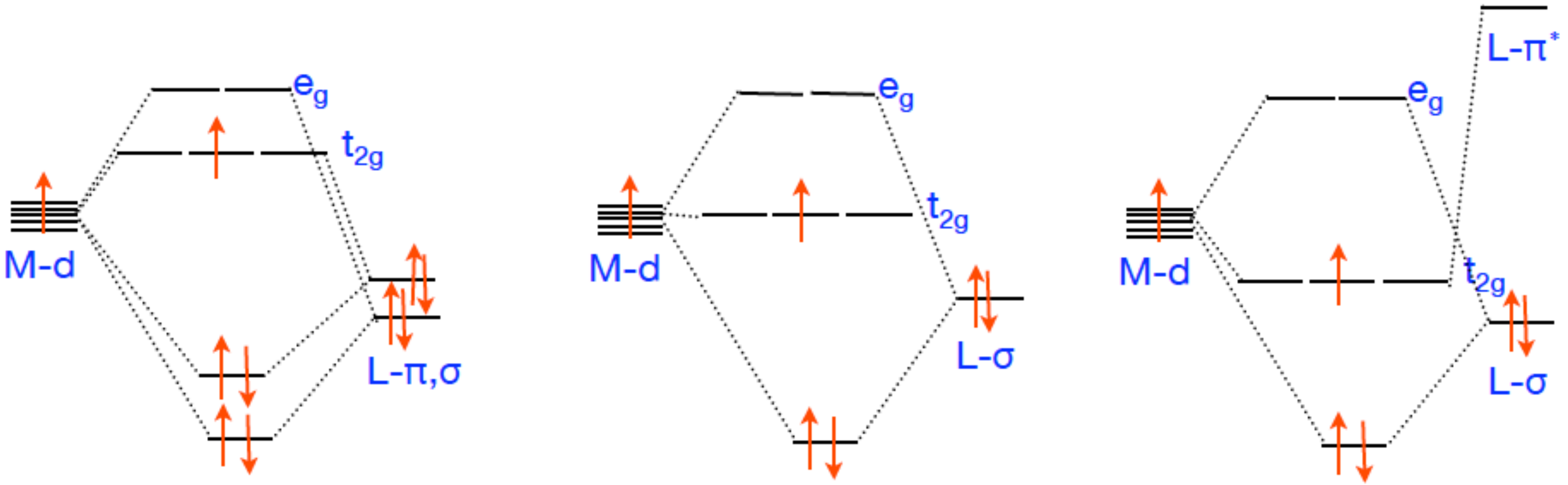
Δ SMALL

Δ LARGE

π-DONOR

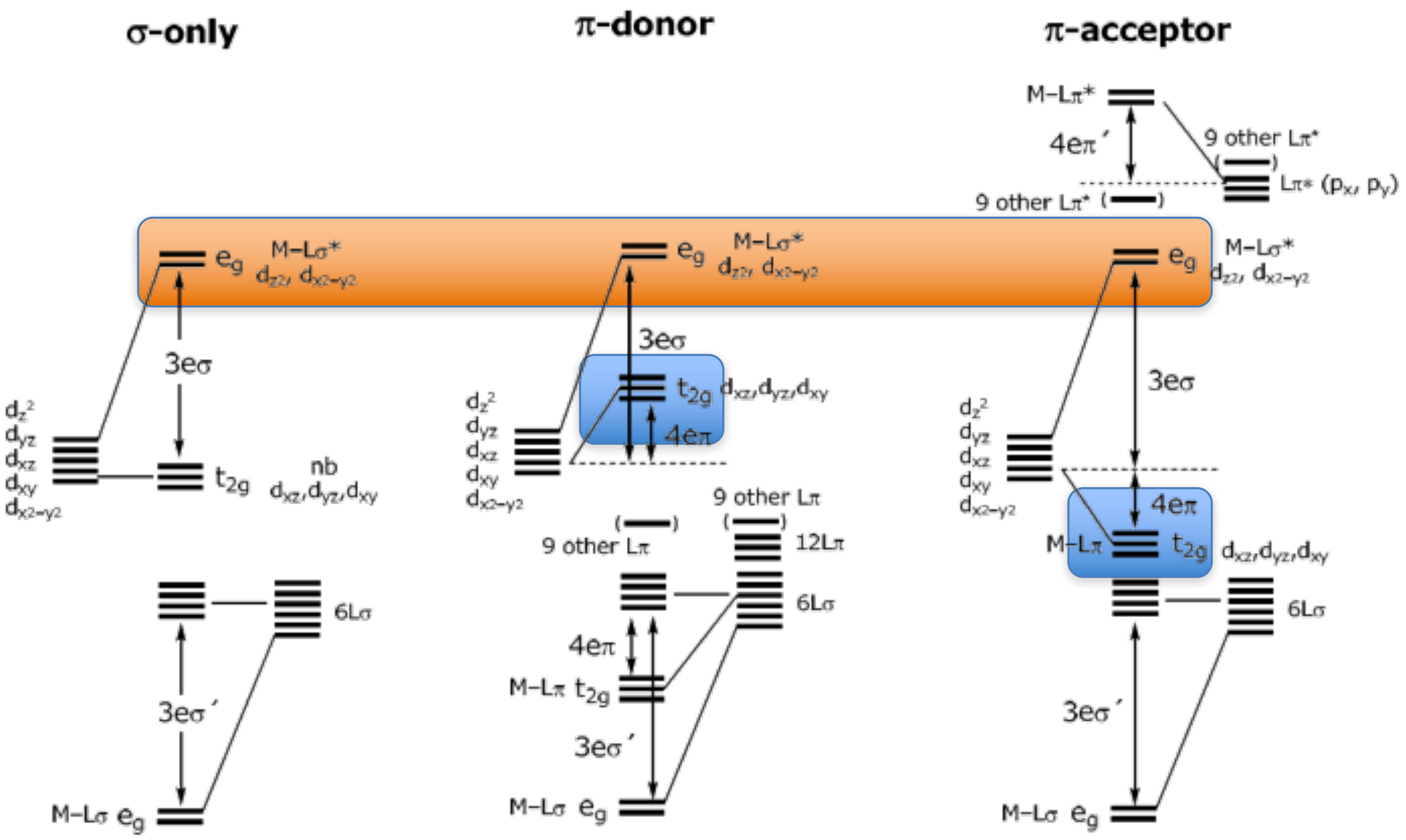
π-'NEUTRAL'

π-ACCEPTOR



MO (LFT) Theory

Summary: π-bonding and π-back bonding modulate the energy of the metal t_{2g} orbitals



MO (LFT) Theory: A Quick Look at Square Planar Complexes

How would the octahedral MO diagram be perturbed if we removed the axial ligands?

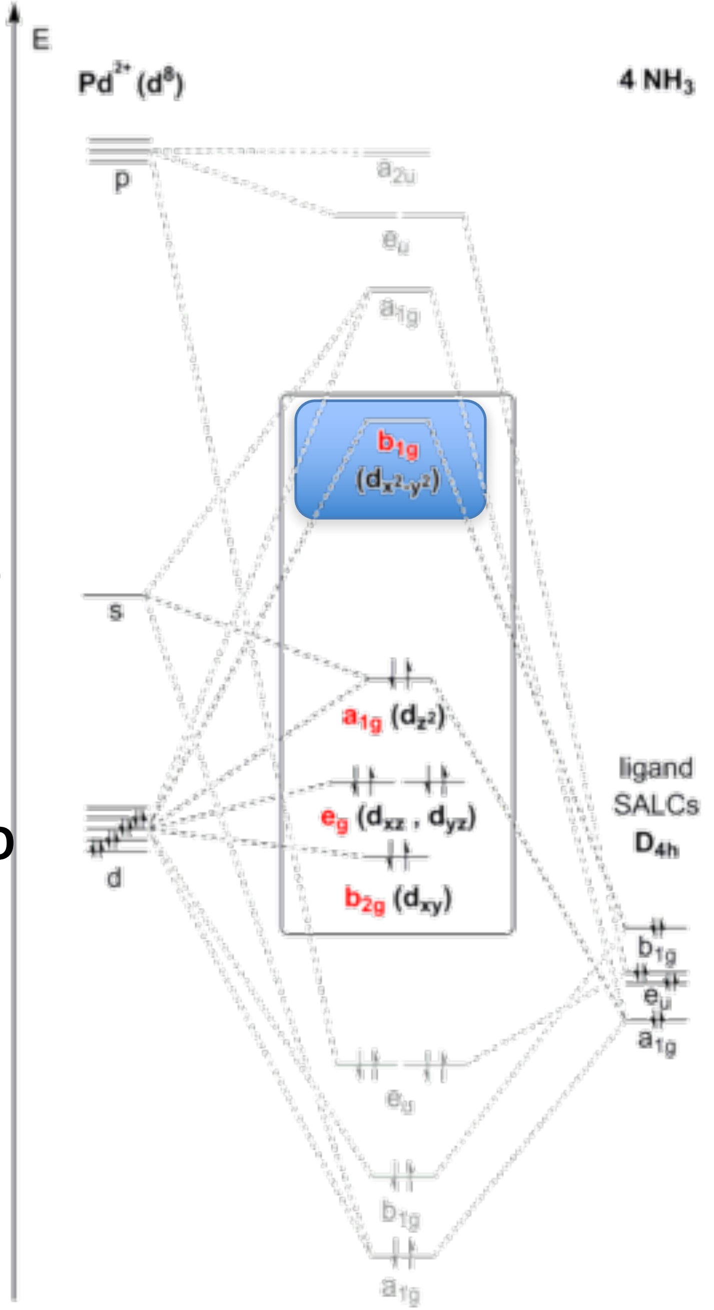
Example
Take $[Pd(NH_3)_4]^{2+}$

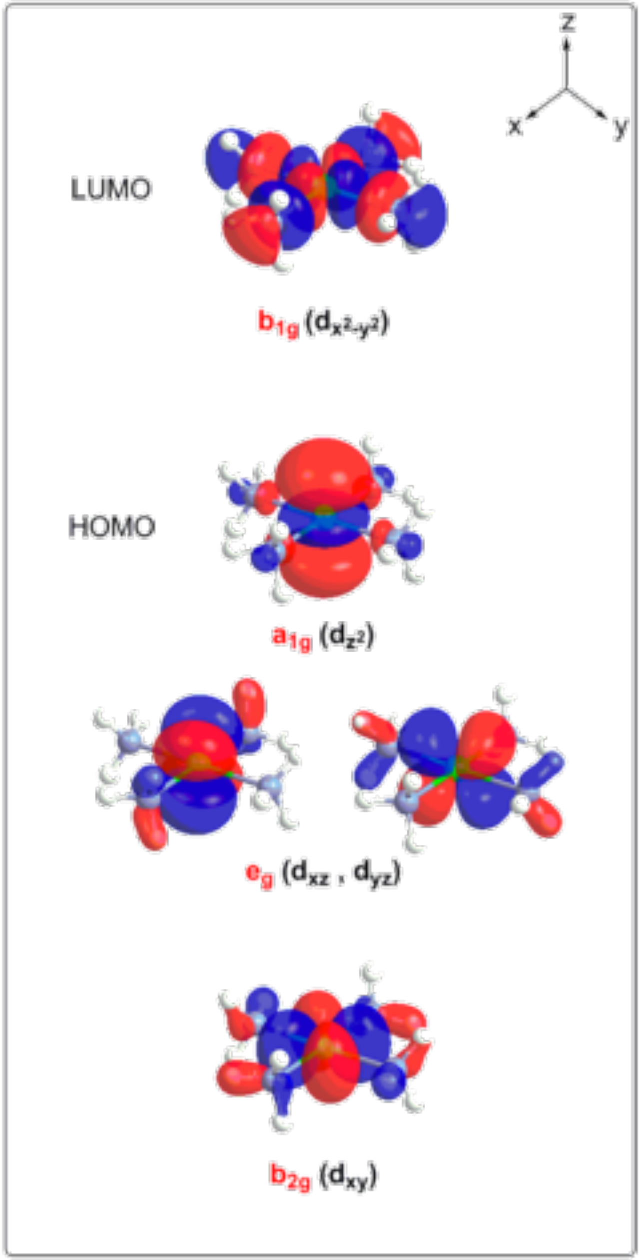
i.e. only σ-donation

The d_{x2-y2} MO (b_{1g}) contains very strong metal–ligand antibonding interactions in the xy plane. It is the **LUMO**

The d_{z2} MO (a_{1g}) contains slight metal–ligand antibonding interactions in the xy plane. It is the **HOMO**

The d_{xy}, d_{xz}, d_{yz}, MO (e_g, b_{2g}) are normally presented as degenerate and non-bonding (no symmetry match with ligand MOs)





MO (LFT) Theory: A Quick Look at Square Planar Complexes

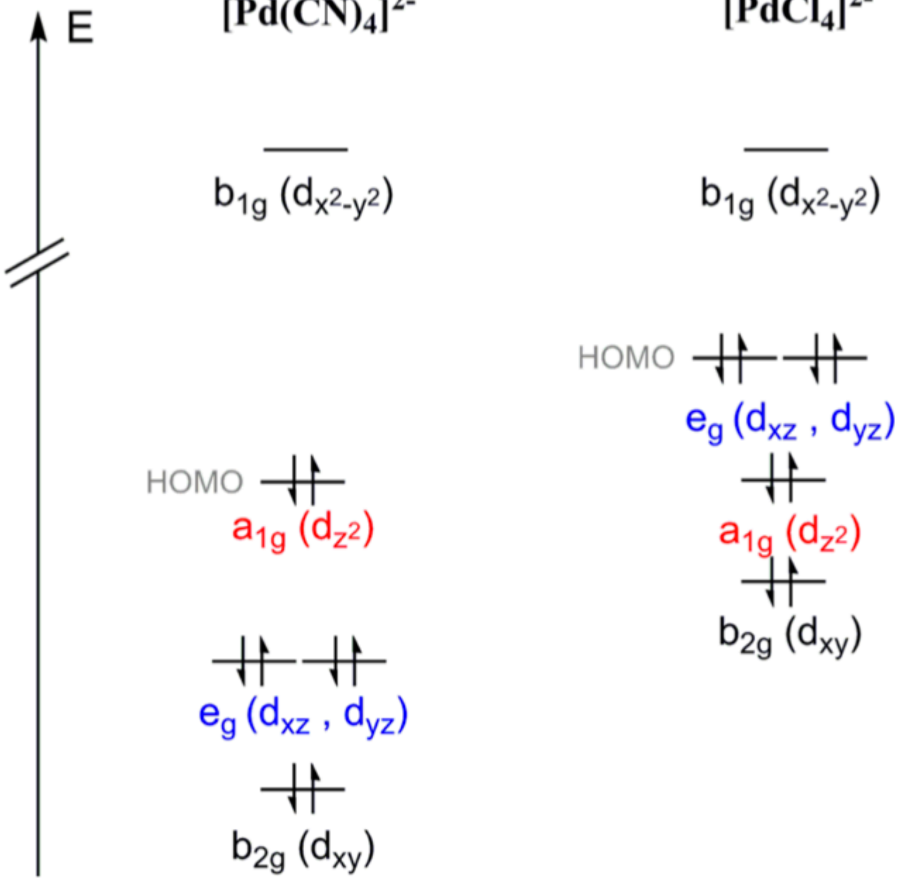
How would the octahedral MO diagram be perturbed if we removed the axial ligands?

What about ligands with π-character?

Including π-interactions results in a re-ordering of the energies of the MOs, unlike what we saw with O_h complexes.

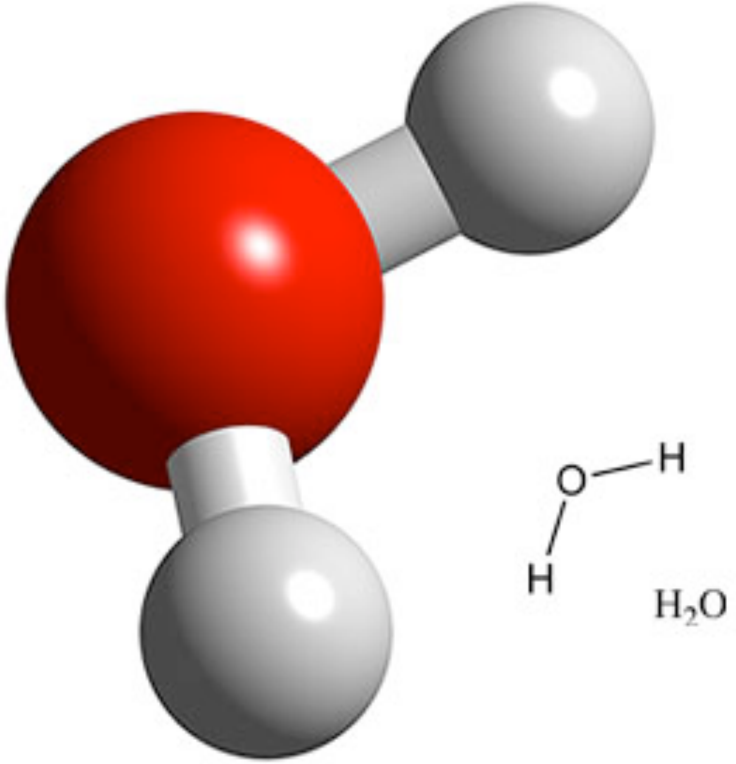
For complexes with p-donating ligands, the HOMO is the e_g MOs and not the a_{1g} MO as a result of the destabilization from π-antibonding interactions with the lone pairs of the ligands.

In addition, the a_{1g} MO is energetically stabilized, due to the weak σ-donating properties of ligands interacting with the metal d_{z2} orbital



Water – The Most Fundamental Ligand

Since water can be viewed as the most fundamental ligand we will use aqueous solutions and the species found therein as the basis for exploring the chemistry



A Summary of Metal Aqua Complexes

green – stable

red – reducing

blue – oxidising

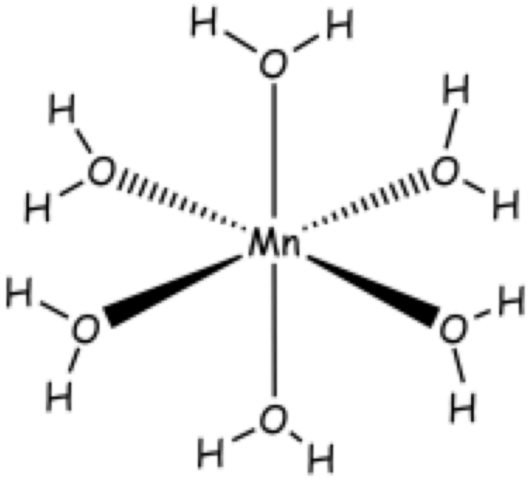
purple - metastable

	II	III	IV	V	VI	VII
Sc	-	$[Sc(OH_2)_7]^{3+}$ d^0				
Ti	$[Ti(OH_2)_6]^{2+}$ d^2	$[Ti(OH_2)_6]^{3+}$ d^1				
V	$[V(OH_2)_6]^{2+}$ d^3	$[V(OH_2)_6]^{3+}$ d^2	$[VO(OH_2)_5]^{2+}$ d^1	$[VO_2(OH_2)_4]^+$ $[VO_4]^{3-}$ d^0		
Cr	$[Cr(OH_2)_6]^{2+}$ d^4	$[Cr(OH_2)_6]^{3+}$ d^3	$[CrO(OH_2)_5]^{2+}$ d^2		$[Cr_2O_7]^{2-}$ $[CrO_4]^{2-}$ d^0	
Mn	$[Mn(OH_2)_6]^{2+}$ d^5	$[Mn(OH_2)_6]^{3+}$ d^4	-	$[MnO_4]^{3-}$ d^2	$[MnO_4]^{2-}$ d^1	$[MnO_4]^-$ d^0
Fe	$[Fe(OH_2)_6]^{2+}$ d^6	$[Fe(OH_2)_6]^{3+}$ d^5	$[FeO(OH_2)_5]^{2+}$ d^4		$[FeO_4]^{2-}$ d^2	
Co	$[Co(OH_2)_6]^{2+}$ d^7	$[Co(OH_2)_6]^{3+}$ d^6	-			
Ni	$[Ni(OH_2)_6]^{2+}$ d^8	-	-			
Cu	$[Cu(OH_2)_n]^{2+}$ d^9 ($n = 5$ or 6)	-	-			
Zn	$[Zn(OH_2)_6]^{2+}$ d^{10}	-	-			

Coordination Geometries

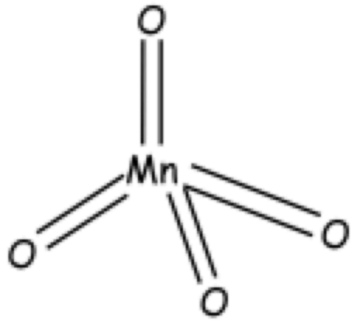
Common

Mn^{2+}



octahedral

MnO_4^-



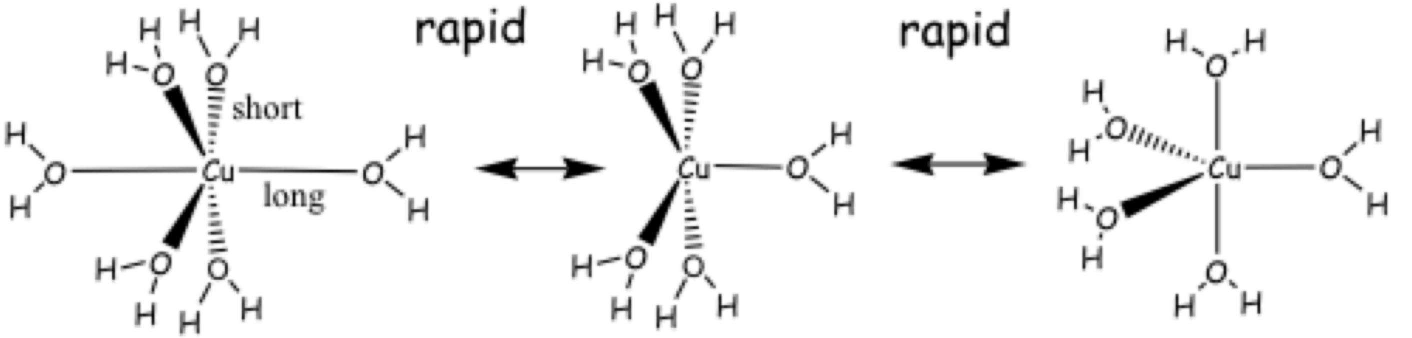
tetrahedral

Coordination Geometries

Unusual

Cu^{2+} d^9

rapid interconversion between 5 and 6 coordination

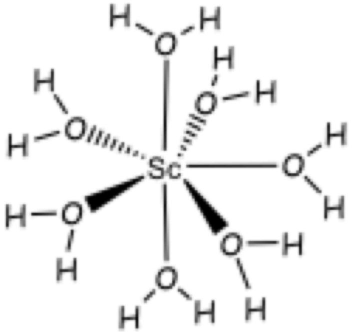


tetragonal - Jahn-Teller distortion

square pyramidal

trigonal bipyramidal

Sc^{3+} (large d^0)

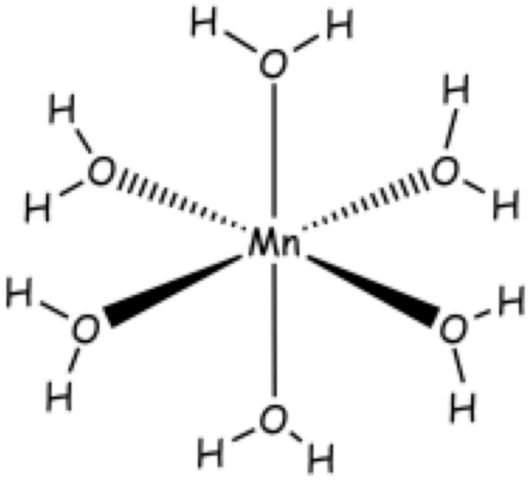


pentagonal bipyramidal

Hydrolysis Chemistry

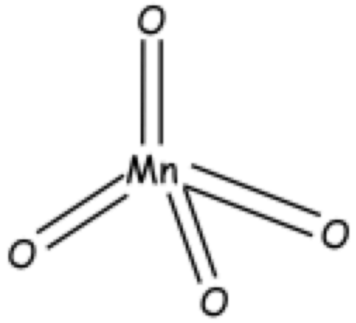
Why does Mn^{II} exist as an aqua complex $[Mn(OH_2)_6]^{2+}$ while Mn^{VII} exists as an oxo complex $[MnO_4]^-$?

Mn^{2+}



octahedral

MnO_4^-

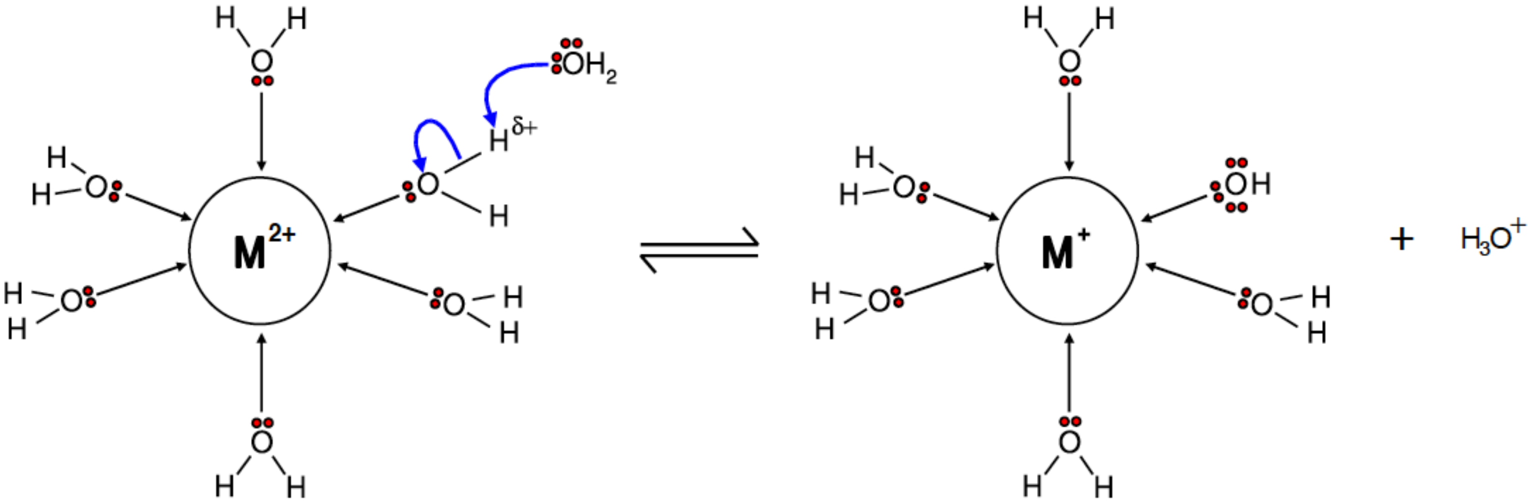


tetrahedral

The Clue lies in the acid-base chemistry

Housecroft and Sharpe, Chapter 7, page 191-193

Hydrolysis Chemistry



- The metal acts as a LA. When H_2O complexes to the metal, the O-H bond is polarized and the proton becomes acidic and so can be abstracted by solvent molecules
- As the charge density increases on the metal, the O-H bond becomes more polarized and the proton acidity increases and more protons are abstracted into solution and the OH_2 ligand becomes an OH^- ligand, **reducing the overall charge of the complex**.
- The solution thus becomes **more acidic**

M^{2+} $[M(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$

Hydrolysis reaction

M^{3+} $[M(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq)$

Hydrolysis Chemistry

- If now a stronger LB is used then more and more protons can be abstracted from metal aqua complexes

$$[M(H_2O)_6]^{2+}(aq) \rightleftharpoons [M(OH)(H_2O)_5]^{+}(aq) \rightleftharpoons [M(OH)_2(H_2O)_4](s) \rightleftharpoons$$

$$[M(OH)_3(H_2O)_3]^{-}{}_{(aq)}(aq) \rightleftharpoons [M(OH)_4(H_2O)_2]^{2-}(aq) \rightleftharpoons M(OH)_5(H_2O)]^{3-}(aq)$$

$$\rightleftharpoons [M(OH)_6]^{4-}(aq)$$

ADD BASE - EQUILIBRIUM MOVES TO THE RIGHT
ADD ACID - EQUILIBRIUM MOVES TO THE LEFT

M^{2+} $$[M(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$$

Hydrolysis reaction

M^{3+} $$[M(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}(aq)$$

Hydrolysis Chemistry

We can determine the relative acidities of $[M(OH_2)_6]^{2+}$ and $[M(OH_2)_6]^{3+}$ ions can be seen below in terms of the respective pKa values

For Fe species:

$$[M(OH_2)_6]^{n+} + H_2O \overset{K_a}{\rightleftharpoons} [M(OH_2)_5OH]^{(n-1)+} + H_3O^+$$

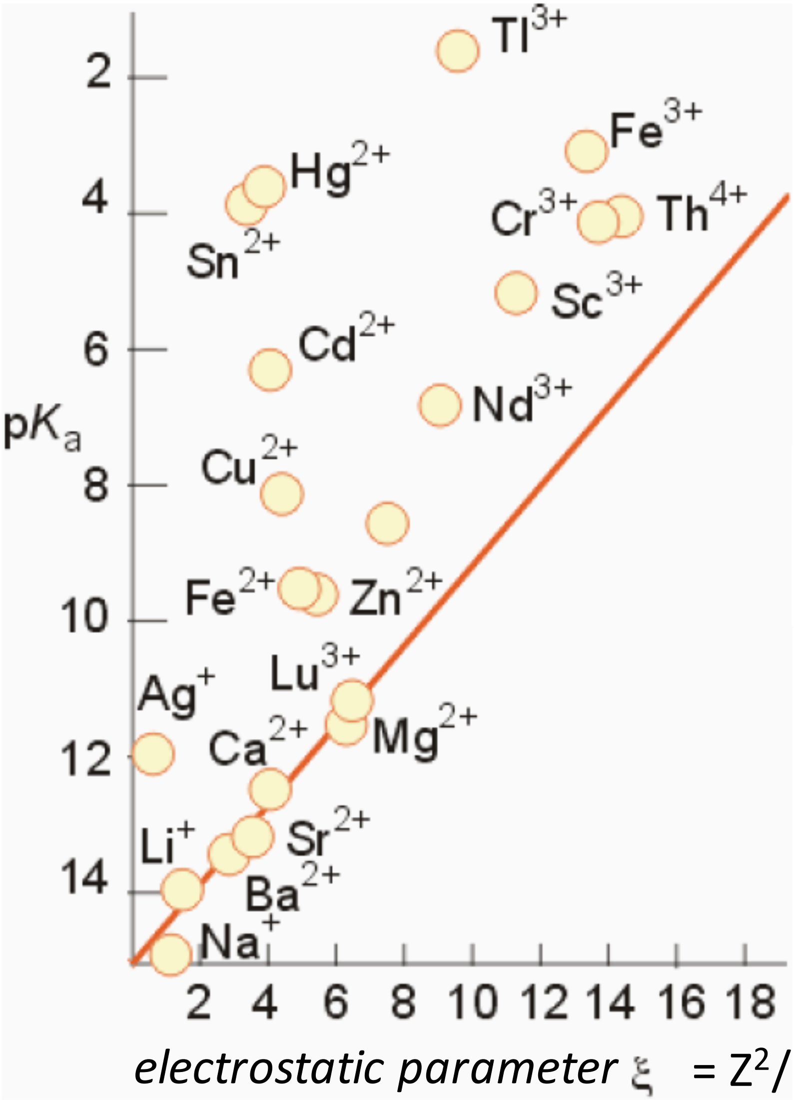
$$K_a = \frac{[M(OH_2)_5OH^{(n-1)+}][H_3O^+]}{[M(OH_2)_6{}^{n+}]} \qquad pK_a = -\log_{10} K_a$$

Fe^{2+} $pK_a = 9.5$

Fe^{3+} $pK_a = 2.2$

The pK_a for $[Fe(OH_2)_6]^{3+}$ is similar to that of formic acid (2.0) – it will liberate CO_2 from carbonate

Hydrolysis Chemistry – pKa Trends



electrostatic parameter ξ = Z^2/r

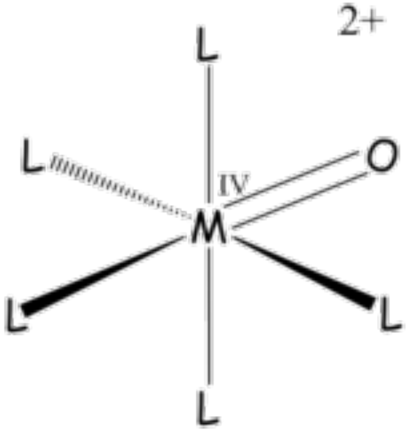
$$pK_a = pH - \log_{10}\frac{[M^{(n-1)+}]}{[M^{n+}]}$$

Empirical relationship that is also based on the electronegativity of the metal

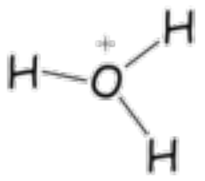
$$pK_a = 15.14 - 0.8816\left\{\frac{Z^2}{r} + 9.60\left(\chi_{Pauling} - 1.50\right)\right\}$$

Hydrolysis Chemistry

If we increase the oxidation state on the metal further (and hence the charge density) we can even render the proton of the hydroxide ligand, O-H$^-$ acidic



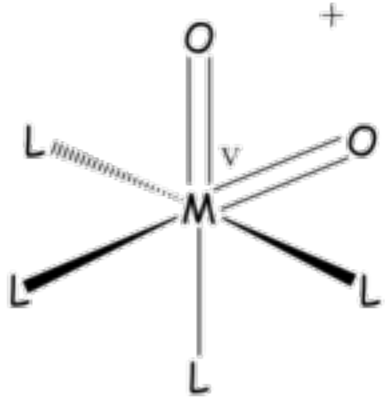
oxo-ion



hydronium ion

Examples:
$[VO(OH_2)_5]^{2+}$,
$[CrO(OH_2)_5]^{2+}$

As the oxidation state on the metal increases further we can obtain multiple oxo groups

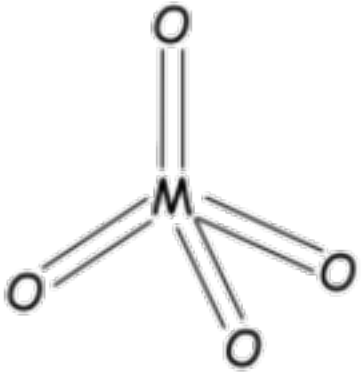


cis-dioxo-ion

Example:
$[VO_2(OH_2)_4]^+$

Hydrolysis Chemistry

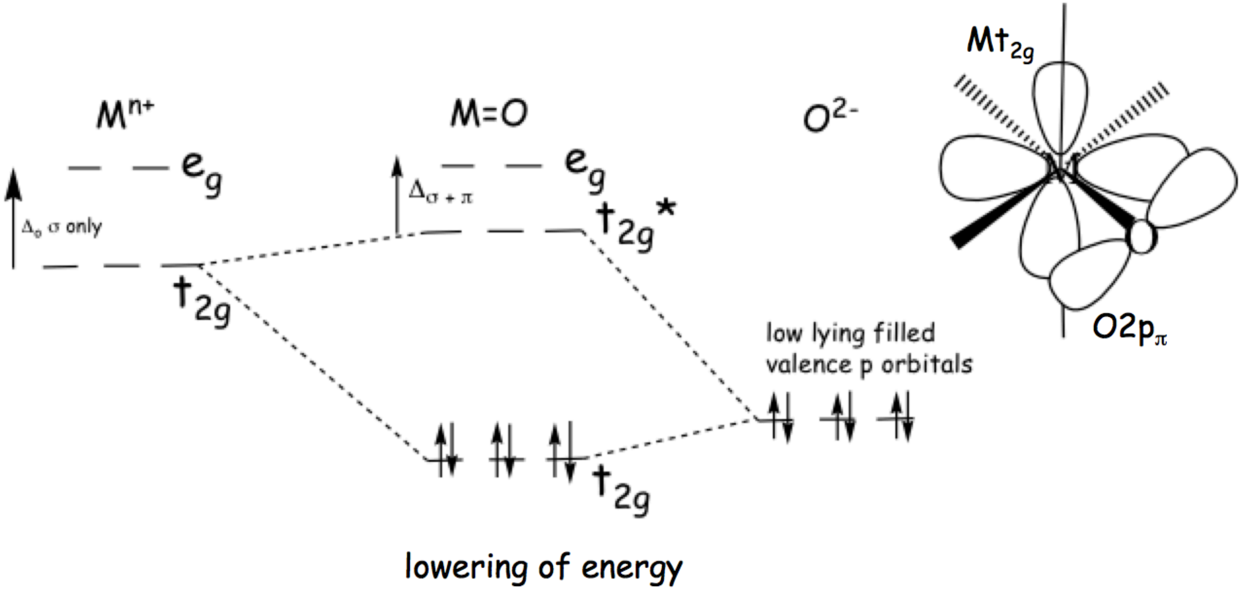
At OS 6+ and greater the **ionic radius becomes too small** to accommodate 6 ligands and thus a 4-coordinate tetrahedral complex is preferred.



Examples: FeO_4^{2-}, MnO_4^-

Oxo groups possess other traits that help to stabilize the resulting metal complex

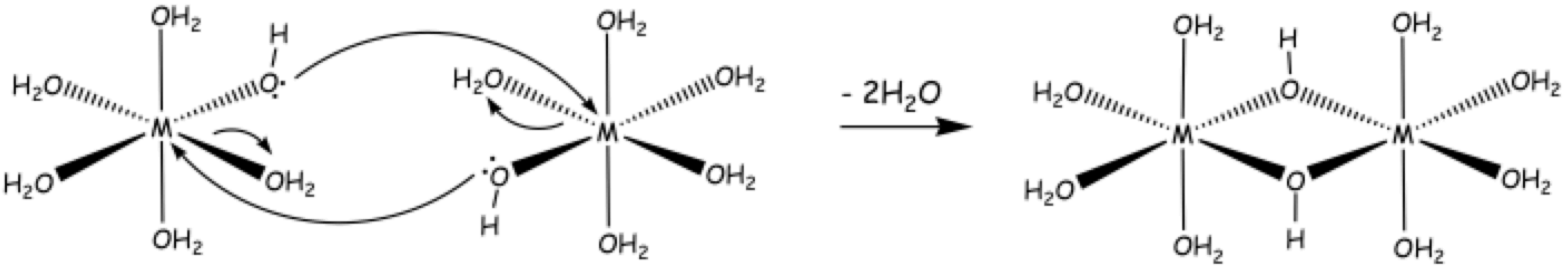
- O^{2-} helps to neutralize high charge on the metal from high OS
- For metals with low d-electron count, strong π-donor ability helps to stabilize t_{2g} orbital



Hydrolysis Chemistry

A further reaction can take place with the trivalent hydroxo ions. They can ‘condense’ together in a process called ‘hydrolytic polymerisation’

Here the OH^- ligand retains a degree of nucleophilicity and substitutes a water on an adjacent ion



dimer

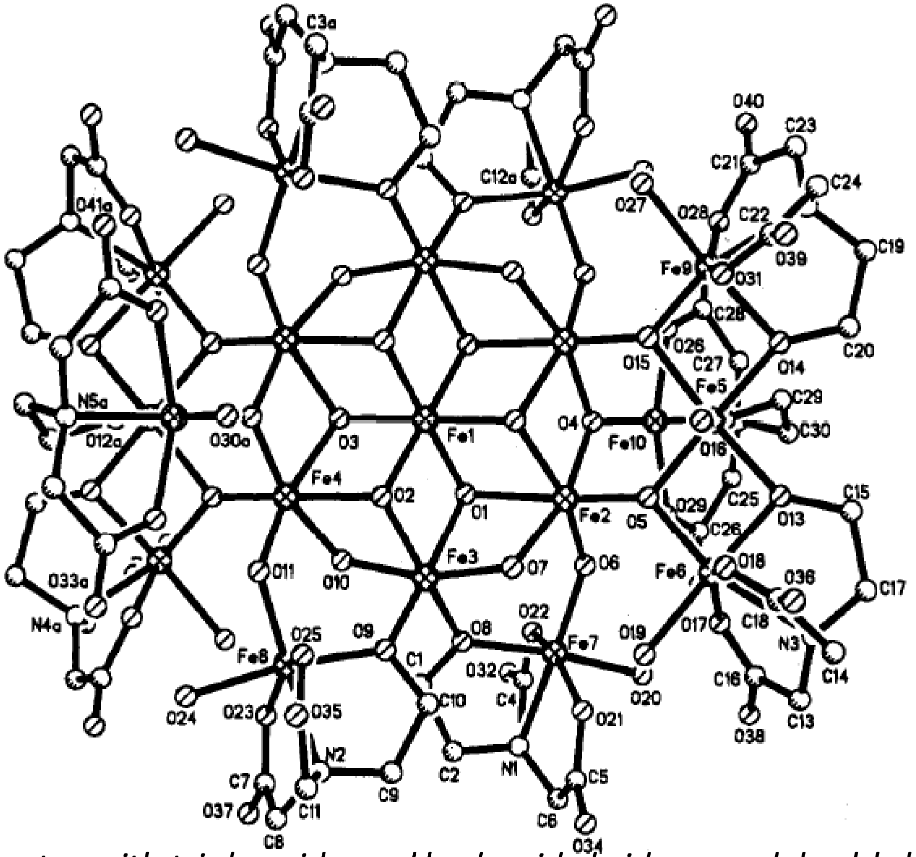
Housecroft and Sharpe, Chapter 7, page 192c

Hydrolysis Chemistry

This process can continue - building up huge OH^- bridged polynuclear structures until solubility limits are exceeded resulting in precipitation of the hydroxide; $M(OH)_3$ aq.

Accompanying dehydration can also occur leading to oxy-hydroxide or oxide (M_2O_3) forms precipitating

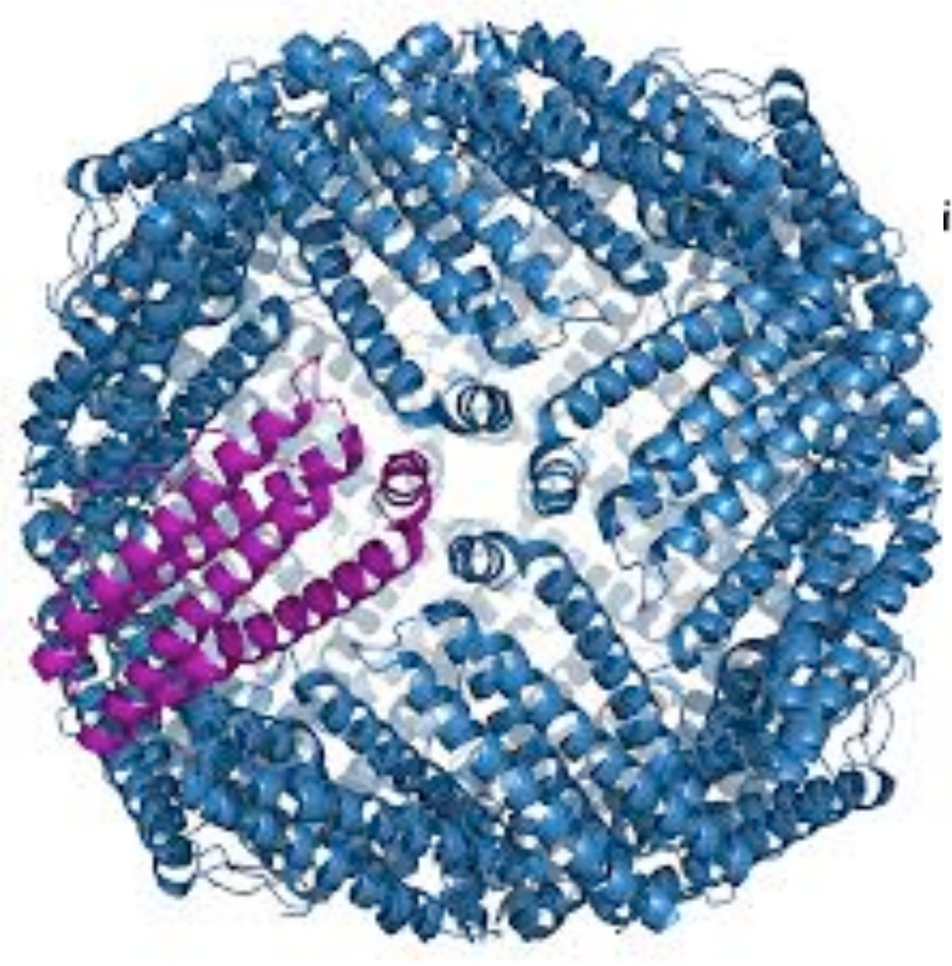
Fe(III) hydrolysis has been well studied and polymeric nanostructures containing over 100 iron atoms have been characterized before $Fe(OH)_3$ precipitation.

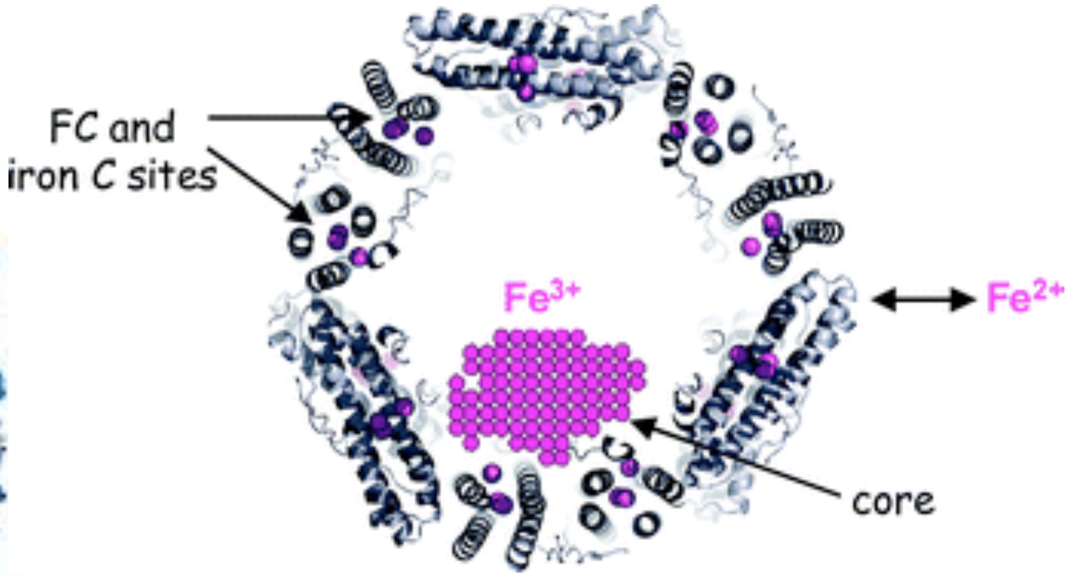


Structure of a Fe_{19} cluster with triply oxide and hydroxide bridges and doubly bridging hydroxides

Hydrolysis Chemistry
Fe Hydrolysis in Action *in vivo*

Ferritin is a protein that stores iron in our body by concentrating it via controlled hydrolysis of Fe^{3+} aq to yield huge oxy-hydroxy bridged nanostructures containing up to 4500 iron atoms.



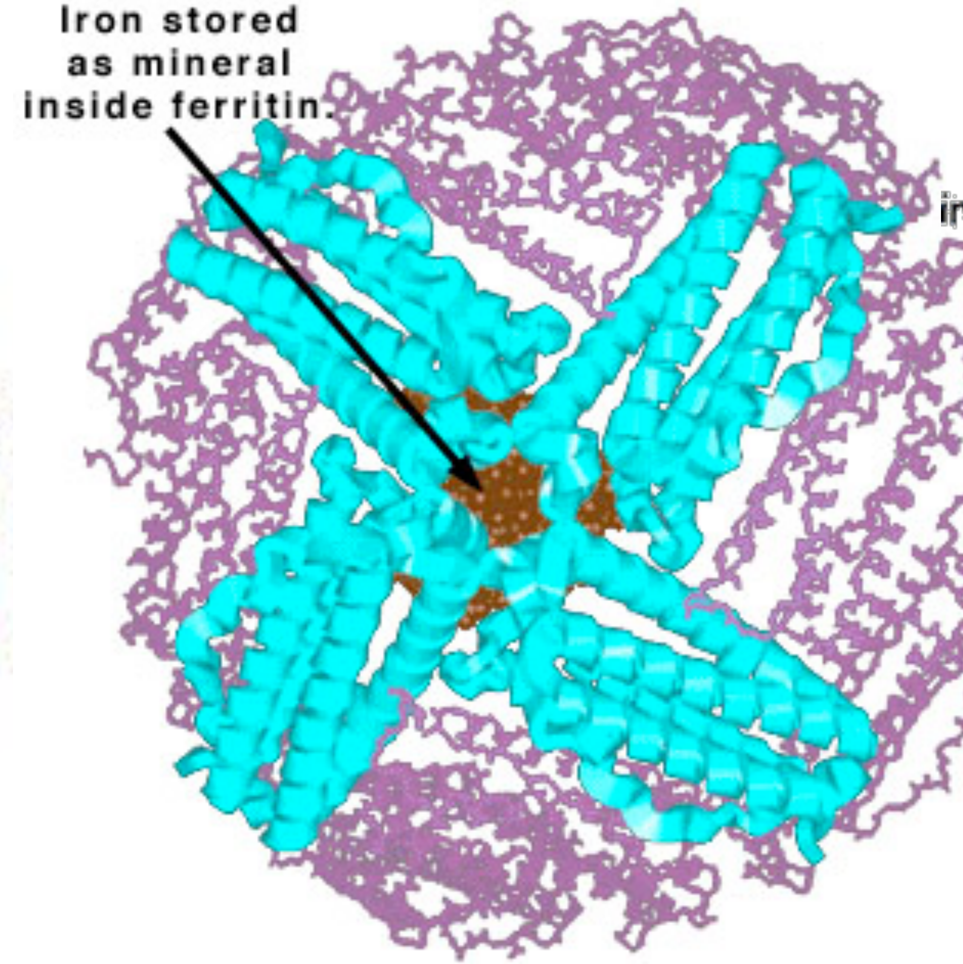


Movement of iron in and out of the protein is achieved via reduction to Fe^{2+}_{aq} which doesn’t hydrolyse at pH 7 and passes through specific M^{2+}-sensing channels

Housecroft and Sharpe, Chapter 29, page 966

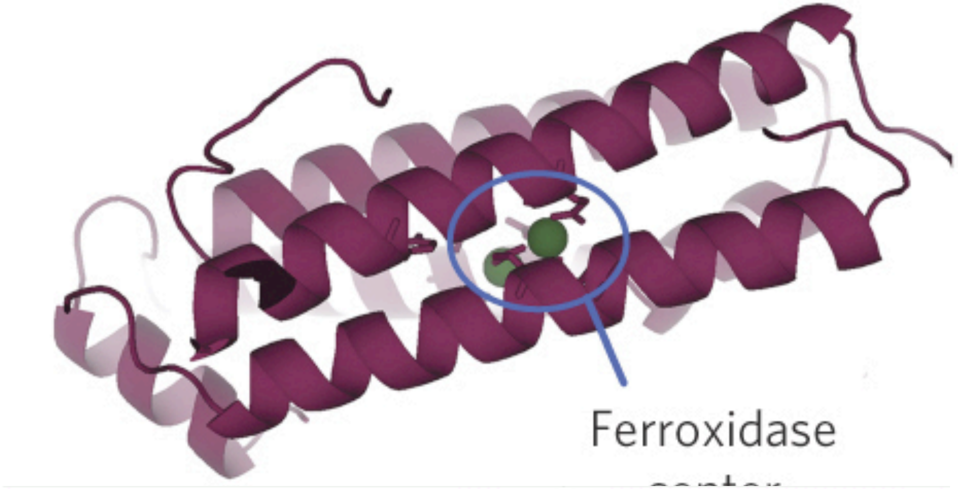
Hydrolysis Chemistry
Fe Hydrolysis in Action *in vivo*

Ferritin is a protein that stores iron in our body by concentrating it via controlled hydrolysis of Fe^{3+}aq to yield huge oxy-hydroxy bridged nanostructures containing up to 4500 iron atoms.

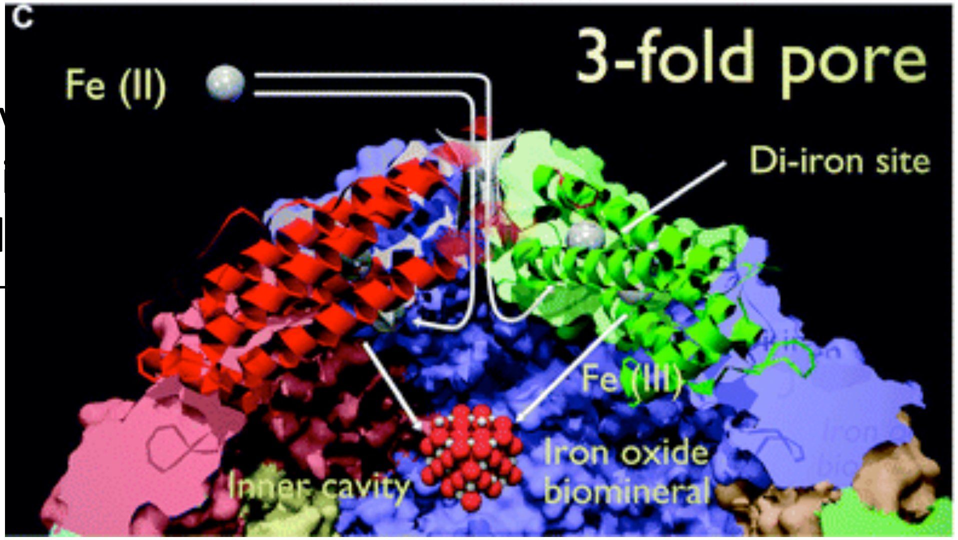


FC
iron

Mov
achi
hyd
M^{2+}



Iron uptake by ferritin



Housecroft and Sharpe, Chapter 29, page 966

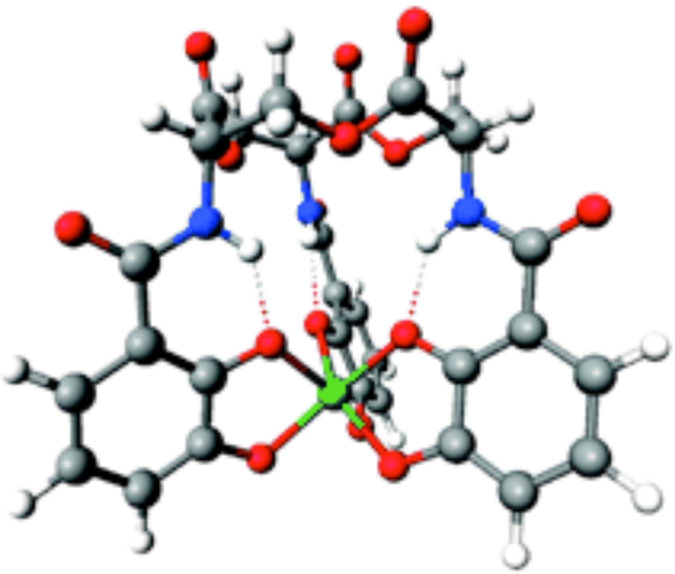
Hydrolysis Chemistry
Fe Hydrolysis in Action *in vivo*

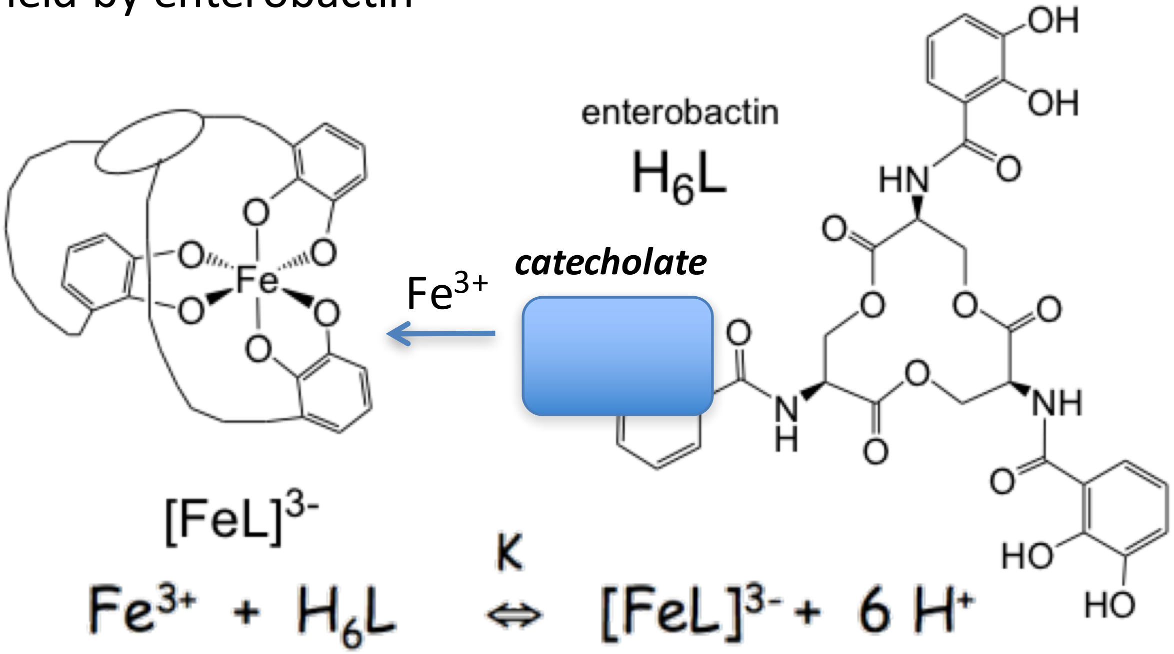
The instability of Fe^{3+} aq solutions at pH 7 with respect to hydrolysis to insoluble $Fe(OH)_3$ ($K_{sp} = 2.6 \times 10^{-39}$) makes it a challenge for biology to concentrate iron in the body.

$K_{sp} = [Fe^{3+}_{aq}]\,[OH^-]^3$

To achieve this, Nature has evolved very powerful agents that bind and solubilize all forms of Fe(III) even $Fe(OH)_3$ to enable efficient iron uptake. These compounds are called **siderophores** *(Greek- iron carrier)*

Some of these have the highest measured equilibrium constants for a metal ion - ligand combination. The record value is held by enterobactin

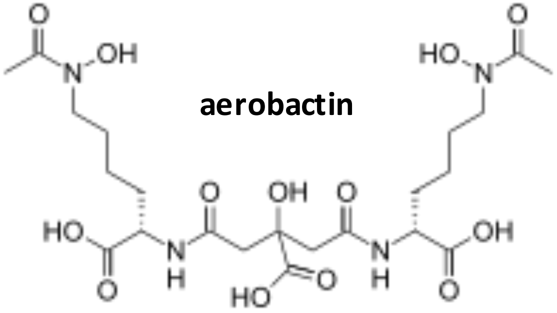




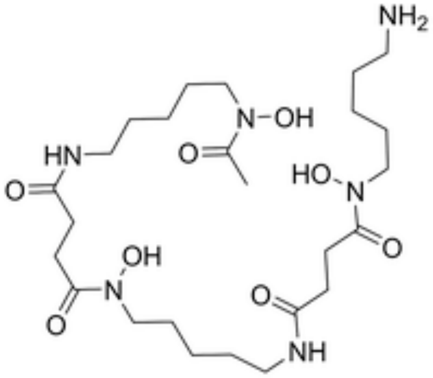
$$Fe^{3+} + H_6L \overset{K}{\Leftrightarrow} [FeL]^{3-} + 6\,H^+$$

Hydrolysis Chemistry
Fe Hydrolysis in Action *in vivo*

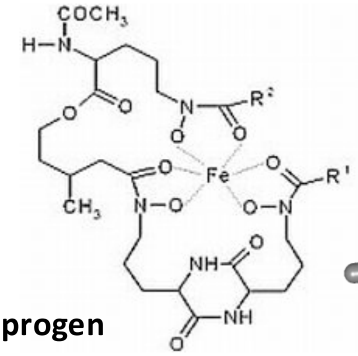
siderophore	donor set	log K
aerobactin	hydroxamate, carboxylate	22.5
coprogen	hydroxamate	30.2
deferrioxamine B	hydroxamate	30.5
ferrichrome	hydroxamate	32.0
Enterobactin	catecholate	49.0



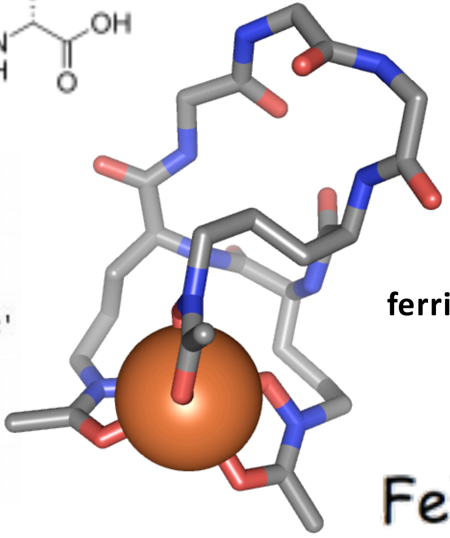
aerobactin



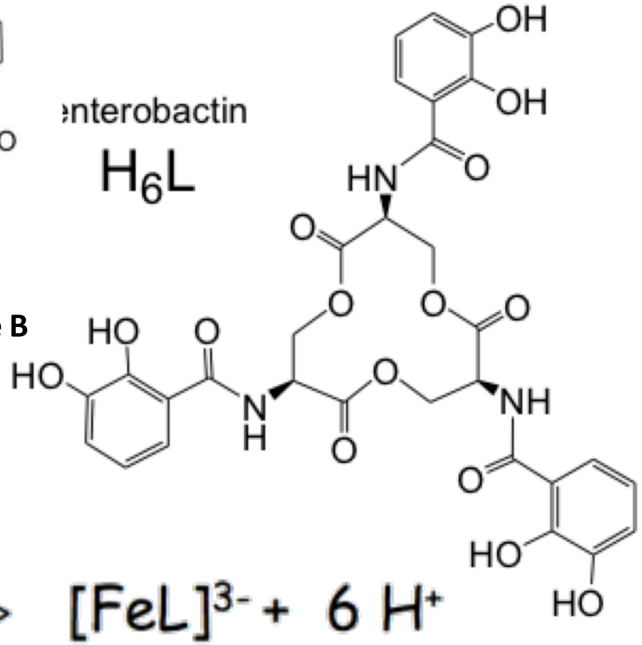
Deferrioxamine B



Coprogen



ferrichrome

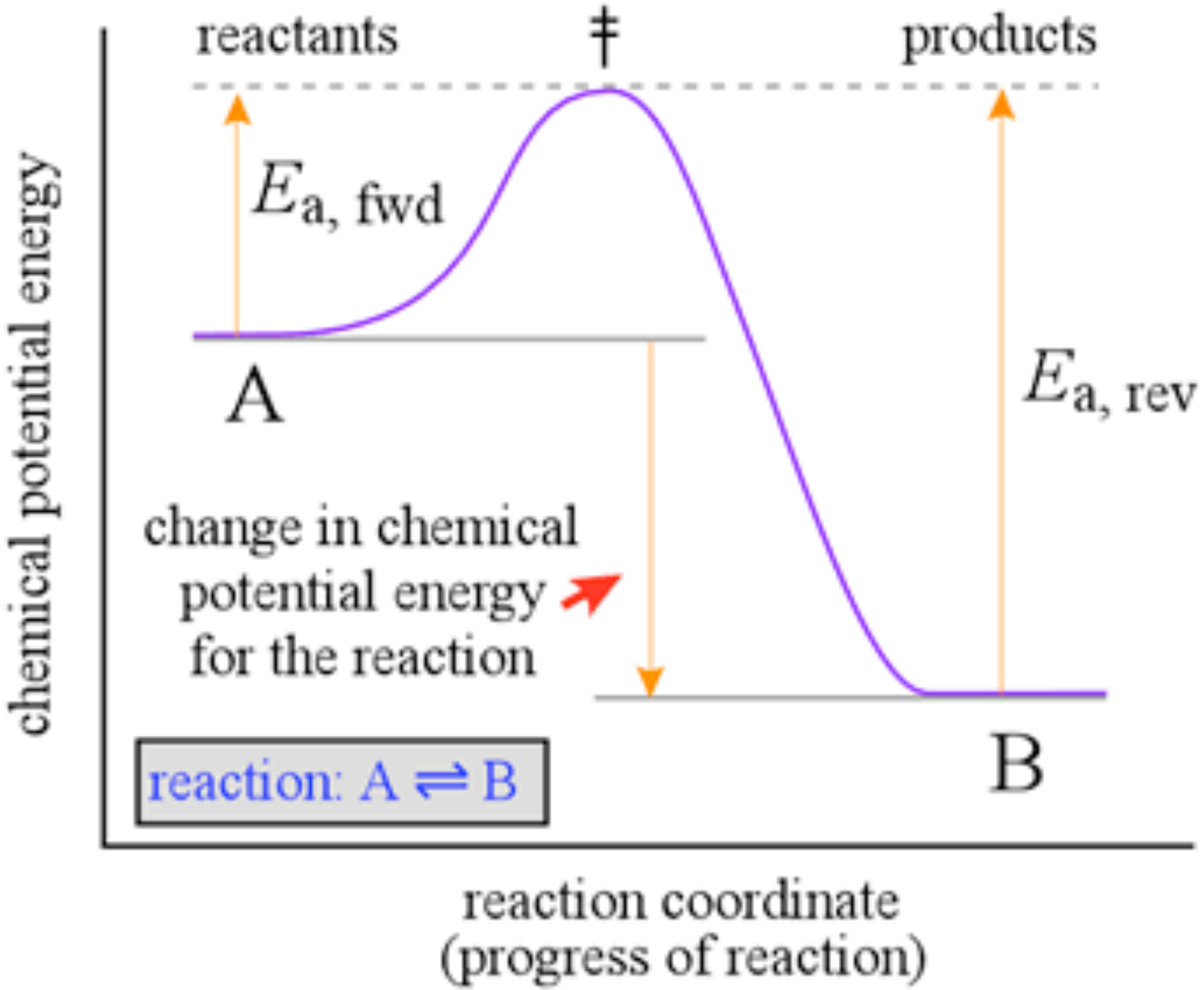


enterobactin

H_6L

$$Fe^{3+} + H_6L \overset{K}{\Leftrightarrow} [FeL]^{3-} + 6\,H^+$$

Thermodynamics of metal complex formation



Housecroft and Sharpe, Chapter 7, page 301

Thermodynamics of metal complex formation

This means processes at **equilibrium**. *e.g.,* hydrolysis, Fe^{3+} complexation with siderophores

Let's look at ligand exchange in more detail by looking at

$[M(OH_2)_6]^{n+} + mL \rightarrow [M(OH_2)_{6-m}mL]^{n+} \rightarrow\rightarrow [M(L)_6]^{n+}$ (L is a neutral ligand)

$$[M(OH_2)_6]^{n+} + L \underset{}{\overset{K_1}{\rightleftharpoons}} [M(OH_2)_5L]^{n+} + H_2O \qquad K_1 = \frac{[M(OH_2)_5L^{n+}]}{[M(OH_2)_6{}^{n+}]\,[L]}$$

$$[M(OH_2)_5L]^{n+} + L \underset{}{\overset{K_2}{\rightleftharpoons}} [M(OH_2)_4L_2]^{n+} + H_2O \qquad K_2 = \frac{[M(OH_2)_4L_2{}^{n+}]}{[M(OH_2)_5L^{n+}]\,[L]}$$

$$\downarrow$$

$$\downarrow$$

$$\downarrow$$

$$[M(OH_2)L_5]^{n+} + L \underset{}{\overset{K_6}{\rightleftharpoons}} [ML_6]^{n+} + H_2O \qquad K_6 = \frac{[ML_6{}^{n+}]}{[M(OH_2)L_5{}^{n+}]\,[L]}$$

K_1-K_6 are know as stepwise stability constants

Thermodynamics of metal complex formation

This means processes at **equilibrium**. *e.g.*, hydrolysis, Fe^{3+} complexation with siderophores

Let's look at ligand exchange in more detail by looking at

$$[M(OH_2)_6]^{n+} + mL \rightarrow [M(OH_2)_{6-m}mL]^{n+} \rightarrow\rightarrow [M(L)_6]^{n+} \text{ (L is a neutral ligand)}$$

We an define an overall stability constant, β, for the complete exchange of H_2O ligands for L

$$[M(OH_2)_6]^{n+} + 6L \overset{\beta_6}{\rightleftharpoons} [ML_6]^{n+} + 6\,H_2O \qquad \beta_6 = \frac{[ML_6{}^{n+}]}{[M(OH_2)_6{}^{n+}]\,[L]^6}$$

$$\beta_6 = K_1{*}K_2{*}K_3{*}K_4{*}K_5{*}K_6$$
$$\log(\beta_6) = \log(K_1) + \log(K_2) + \log(K_3) + \log(K_4) + \log(K_5) + \log(K_6)$$

What this implies is that $\boldsymbol{\beta_6 > \beta_5 > \beta_4 > \beta_3 > \beta_2 > \beta_1}$ and so there will always be complete substitution of L for H_2O

Thermodynamics of metal complex formation

An example: NH_3 replacing H_2O on $[Ni(OH_2)_6]^{2+}$

$-\log K_1$	**$-\log K_2$**	**$-\log K_3$**	**$-\log K_4$**	**$-\log K_5$**	**$-\log K_6$**
-2.79	-2.26	-1.69	-1.25	-0.74	-0.03

Note the steady fall in K_n

What this data means is that $[Ni(OH_2)_6]^{2+}$ + excess NH_3 gives only $[Ni(NH_3)_6]^{2+}$

$\log \beta_6 = 2.79 + 2.26 + 1.69 + 1.25 + 0.74 + 0.03 = 8.76$
$\beta_6 = 5.75 \times 10^8$

Thermodynamics of metal complex formation

An example: NH_3 replacing H_2O on $[Ni(OH_2)_6]^{2+}$

With known equilibrium constants, K_n, we can determine free energy ΔG_n

$\Delta G_n = -RT \ln(K_n)$, where R is the gas constant 8.314 J mol^{-1} K^{-1}

So at 303 K, $\Delta G_1 = -(8.314 \times 10^{-3} * 303) \ln(10^{2.79}) = \mathbf{-16.2\ KJ\ mol^{-1}}$

$\Delta G_n = \Delta H_n - T\Delta S_n$

If $\Delta H_1 = \mathbf{-16.8\ KJ\ mol^{-1}}$
$\Delta S_1 = (\Delta H_1 - \Delta G_1)/T = [-16.8-(-16.2)]/303 = \mathbf{-1.98\ J\ mol^{-1}\ K^{-1}}$

Quite small – no change in # molecules

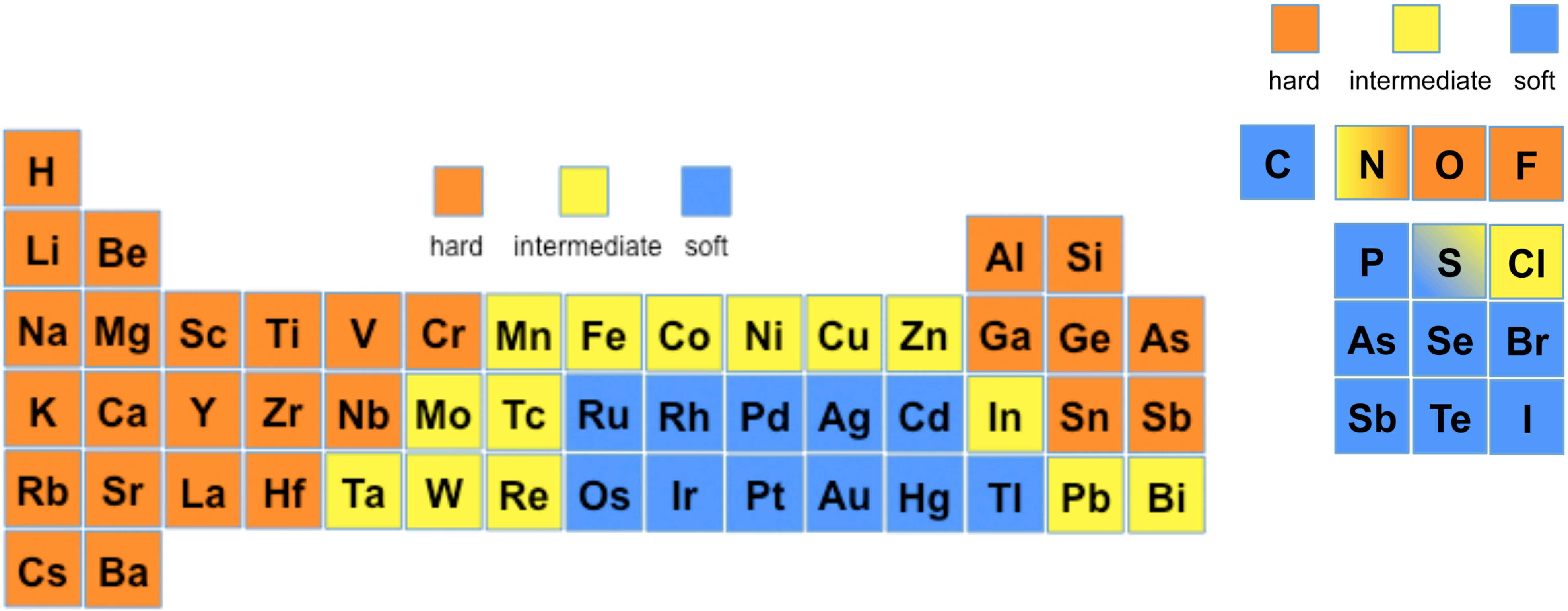
Therefore substitution is primarily an **enthalpic effect** (ΔH is governing the process)
This is due to the stronger Ni^{2+}-N bonds being formed compared to the Ni^{2+}-O bonds (more exothermic)

Thermodynamics of metal complex formation
HSAB Theory

An example: NH_3 replacing H_2O on $[Ni(OH_2)_6]^{2+}$

Now why is N a more preferred donor than O for Ni^{2+}?

The answer lies in **Hard-Soft Acid and Base Theory (HSAB)**

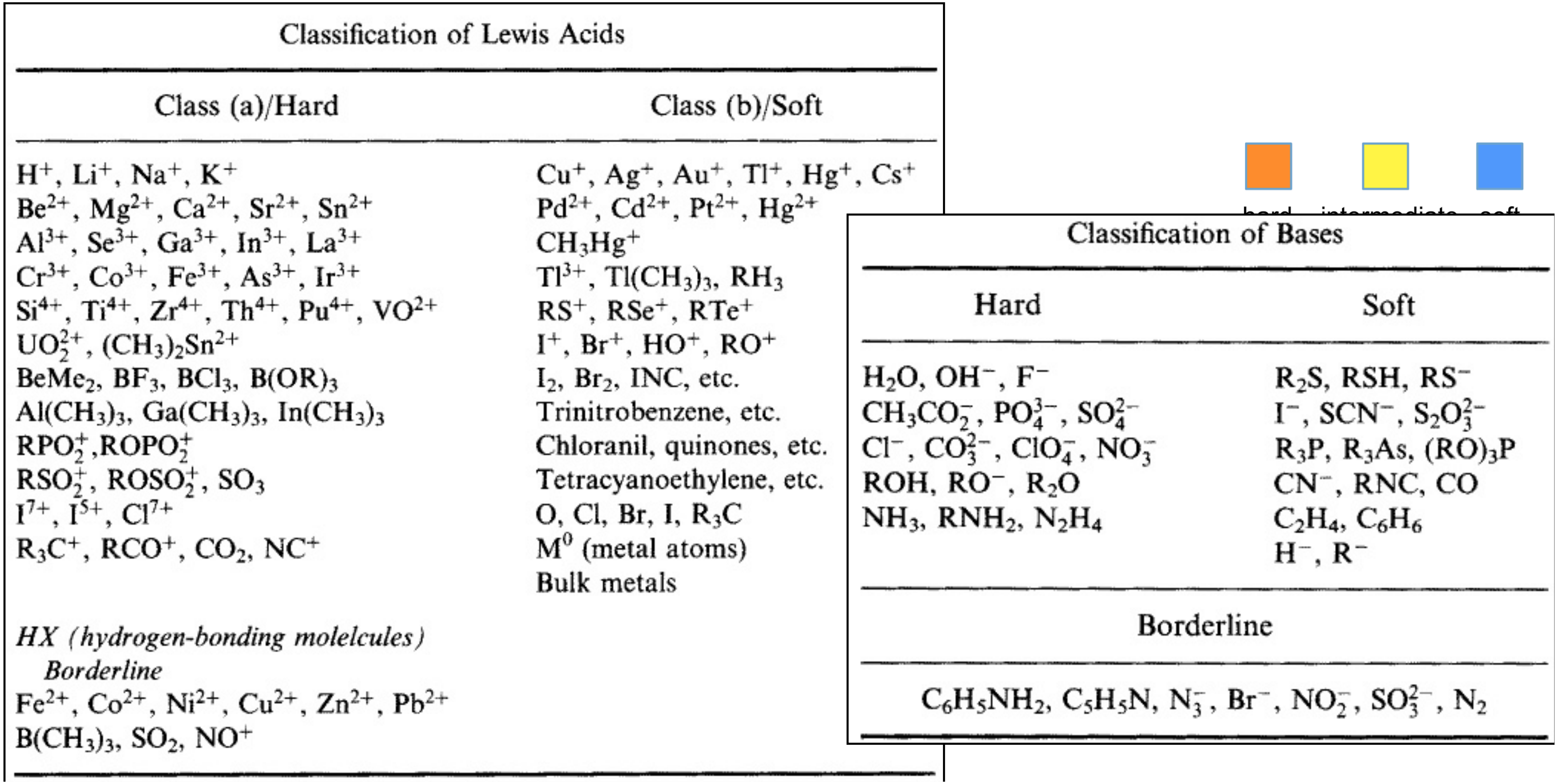


Housecroft and Sharpe, Chapter 7, page 206

Thermodynamics of metal complex formation
HSAB Theory

Salem-Klopman Equation (simplified)

$$\Delta E = -\underbrace{\frac{Q_{nuc}Q_{elec}}{\varepsilon R}}_{\text{second term}} + \underbrace{\frac{2(c_{nuc}c_{elec}\beta)^2}{E_{HOMO} - E_{LUMO}}}_{\text{third term}}$$



Classification of Lewis Acids

Class (a)/Hard	Class (b)/Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}	CH_3Hg^+
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}	Tl^{3+}, $Tl(CH_3)_3$, RH_3
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}, VO^{2+}	RS^+, RSe^+, RTe^+
UO_2^{2+}, $(CH_3)_2Sn^{2+}$	I^+, Br^+, HO^+, RO^+
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	I_2, Br_2, INC, etc.
$Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$	Trinitrobenzene, etc.
RPO_2^+,$ROPO_2^+$	Chloranil, quinones, etc.
RSO_2^+, $ROSO_2^+$, SO_3	Tetracyanoethylene, etc.
I^{7+}, I^{5+}, Cl^{7+}	O, Cl, Br, I, R_3C
R_3C^+, RCO^+, CO_2, NC^+	M^0 (metal atoms)
	Bulk metals
HX (hydrogen-bonding molelcules)	
Borderline	
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	
$B(CH_3)_3$, SO_2, NO^+	

🟧 hard 🟨 intermediate 🟦 soft

Classification of Bases

Hard	Soft
H_2O, OH^-, F^-	R_2S, RSH, RS^-
$CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}	I^-, SCN^-, $S_2O_3^{2-}$
Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-	R_3P, R_3As, $(RO)_3P$
ROH, RO^-, R_2O	CN^-, RNC, CO
NH_3, RNH_2, N_2H_4	C_2H_4, C_6H_6
	H^-, R^-

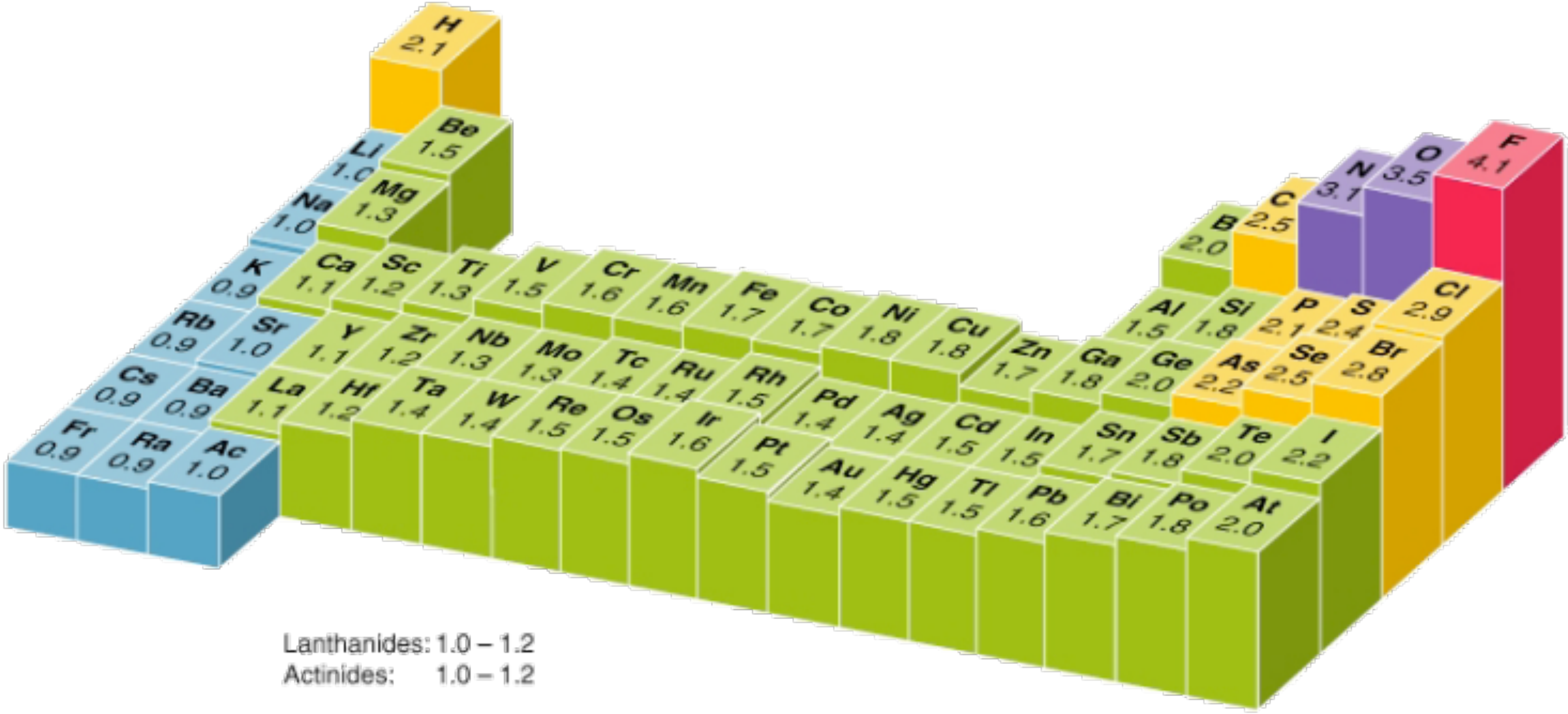
Borderline

$C_6H_5NH_2$, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}, N_2

Thermodynamics of metal complex formation
HSAB Theory

Salem-Klopman Equation (simplified)

$$\Delta E = -\underbrace{\frac{Q_{nuc}Q_{elec}}{\varepsilon R}}_{\text{second term}} + \underbrace{\frac{2(c_{nuc}c_{elec}\beta)^2}{E_{HOMO} - E_{LUMO}}}_{\text{third term}}$$



Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

Thermodynamics of metal complex formation
HSAB Theory

Salem-Klopman Equation (simplified)

$$\Delta E = -\underbrace{\frac{Q_{nuc}Q_{elec}}{\varepsilon R}}_{\text{second term}} + \underbrace{\frac{2(c_{nuc}c_{elec}\beta)^2}{E_{HOMO} - E_{LUMO}}}_{\text{third term}}$$

Consider the following examples involving replacement of water by halide ions

$$Fe^{3+}{}_{aq} + X^- \overset{K_1}{\rightleftharpoons} FeX^{2+}{}_{aq} + H_2O$$

$$Hg^{2+}{}_{aq} + X^- \rightleftharpoons HgX^{2+}{}_{aq} + H_2O$$

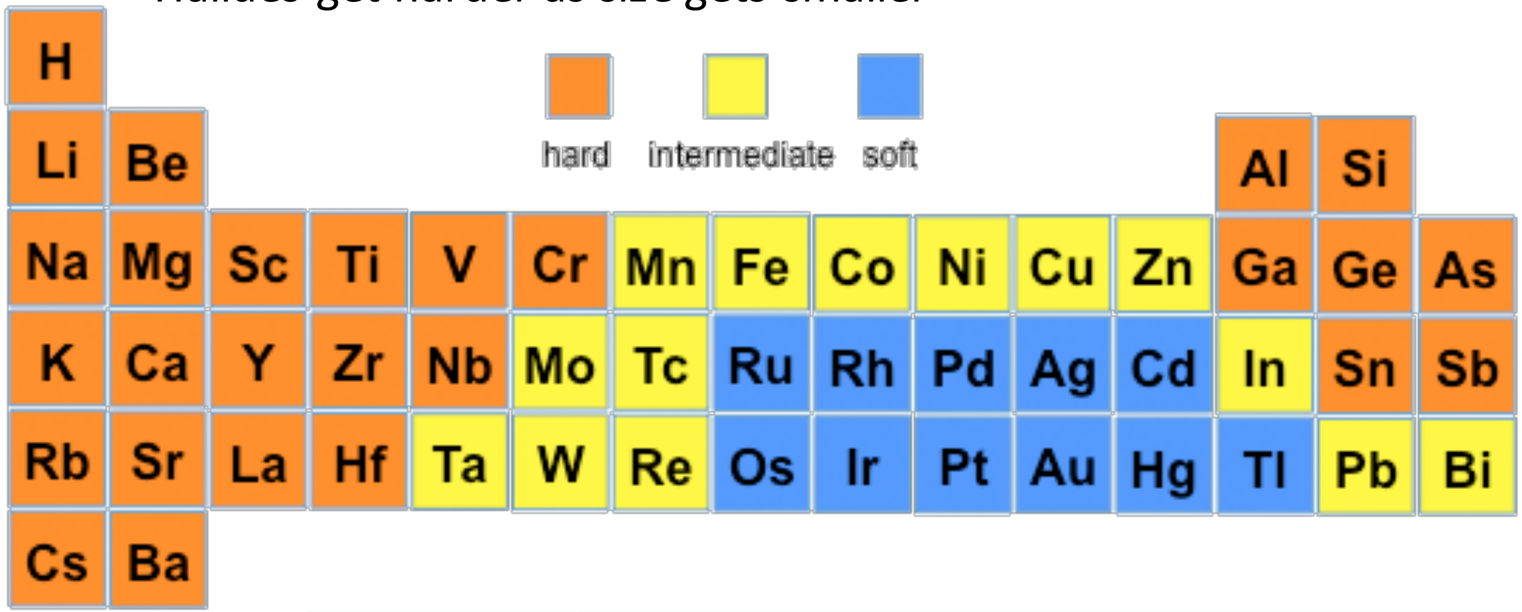
Metal Ion	$\log_{10}K_1$			
	X = F	X = Cl	X = Br	X = I
$Fe^{3+}{}_{aq}$	6.0	1.4	0.5	
$Hg^{2+}{}_{aq}$	1.0	6.7	8.9	12.9

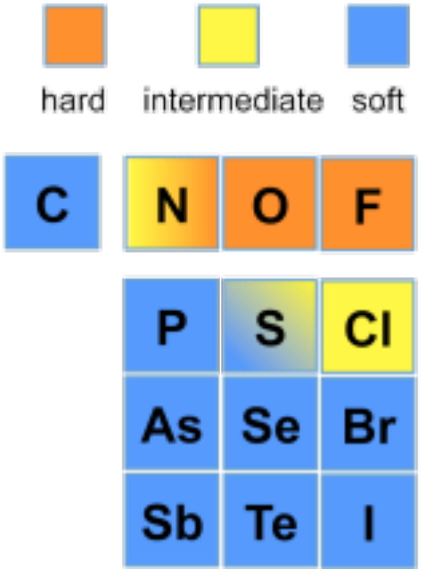
Note the vastly different trends in log K values!

Thermodynamics of metal complex formation
HSAB Theory

$Fe^{3+}{}_{aq}$ is HARD
$Hg^{2+}{}_{aq}$ is SOFT
Halides get harder as size gets smaller

The golden rule:
Strongest M-L interactions require HH or SS match





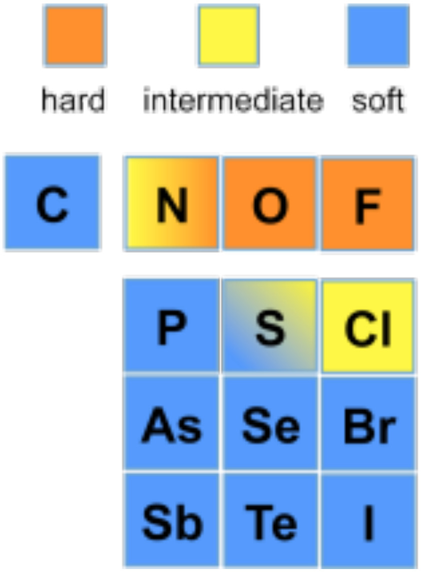
Metal Ion	**$log_{10}K_1$**			
	X = F	**X = Cl**	**X = Br**	**X = I**
$Fe^{3+}{}_{aq}$	6.0	1.4	0.5	
$Hg^{2+}{}_{aq}$	1.0	6.7	8.9	12.9

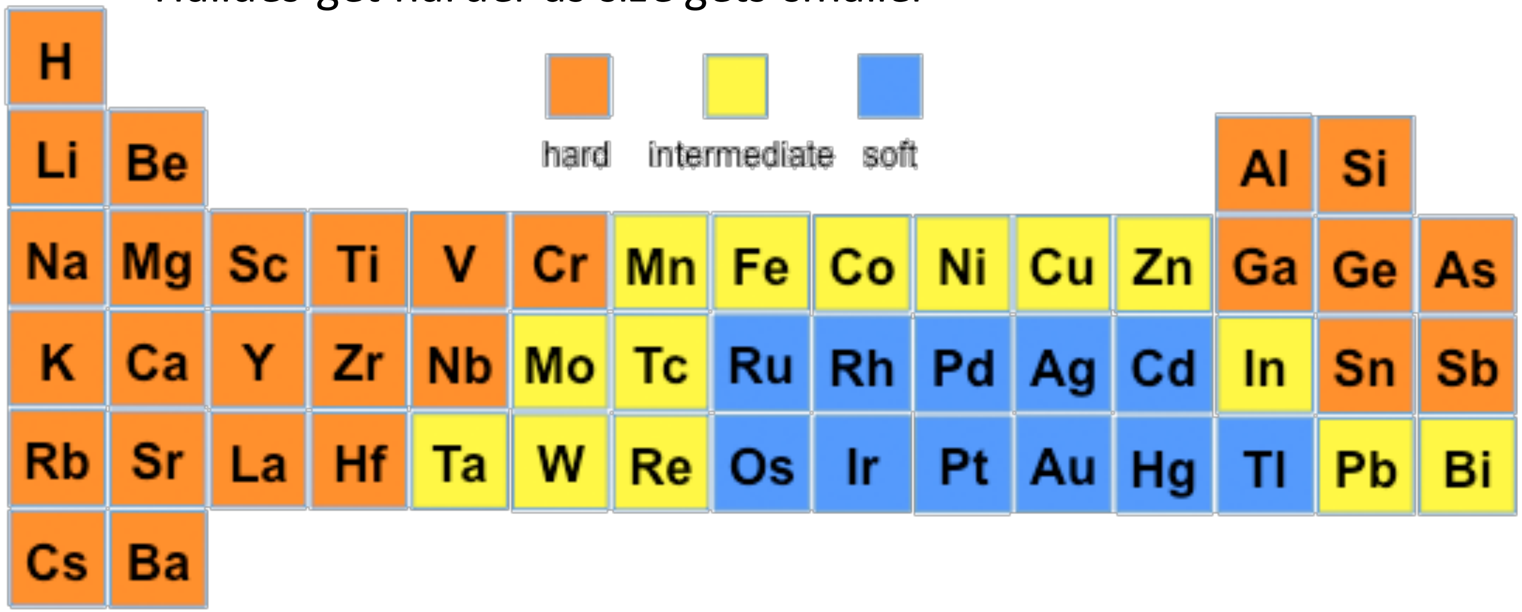
Note the vastly different trends in log K values!

Thermodynamics of metal complex formation
HSAB Theory

Fe^{3+}_{aq} is HARD
Hg^{2+}_{aq} is SOFT
Halides get harder as size gets smaller

The golden rule:
Strongest M-L interactions require HH or SS match





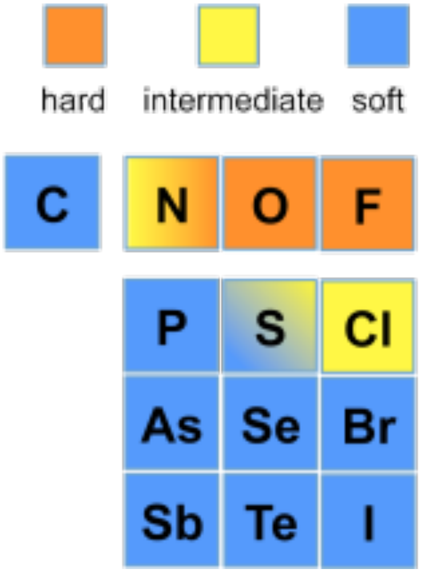
The behaviour of Fe^{3+}_{aq} is paralleled by similar behaviour shown by the Group 1 and 2 metals and the early 3d transition elements to the left

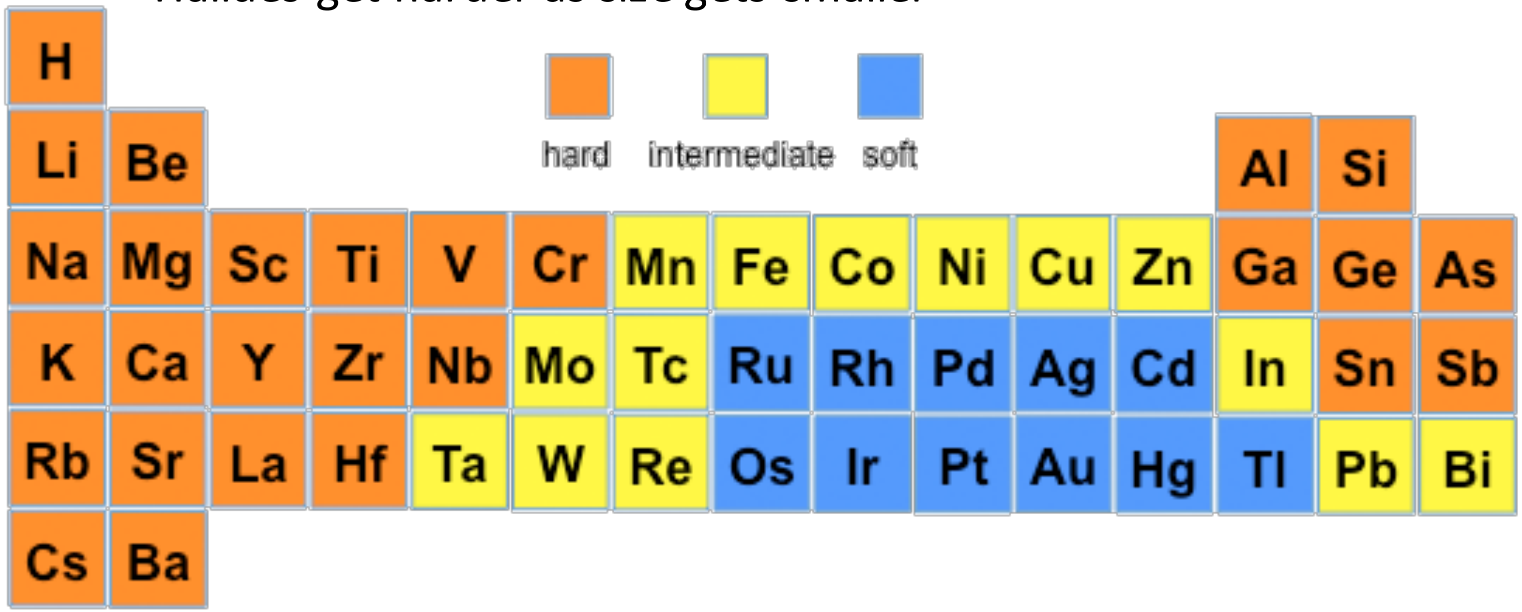
The behaviour of Hg^{2+}_{aq} is paralleled by similar behaviour shown by the heavier p–block elements and the heavier transition elements to the right

Thermodynamics of metal complex formation
HSAB Theory

Fe^{3+}_{aq} is HARD
Hg^{2+}_{aq} is SOFT
Halides get harder as size gets smaller

The golden rule:
Strongest M-L interactions require HH or SS match





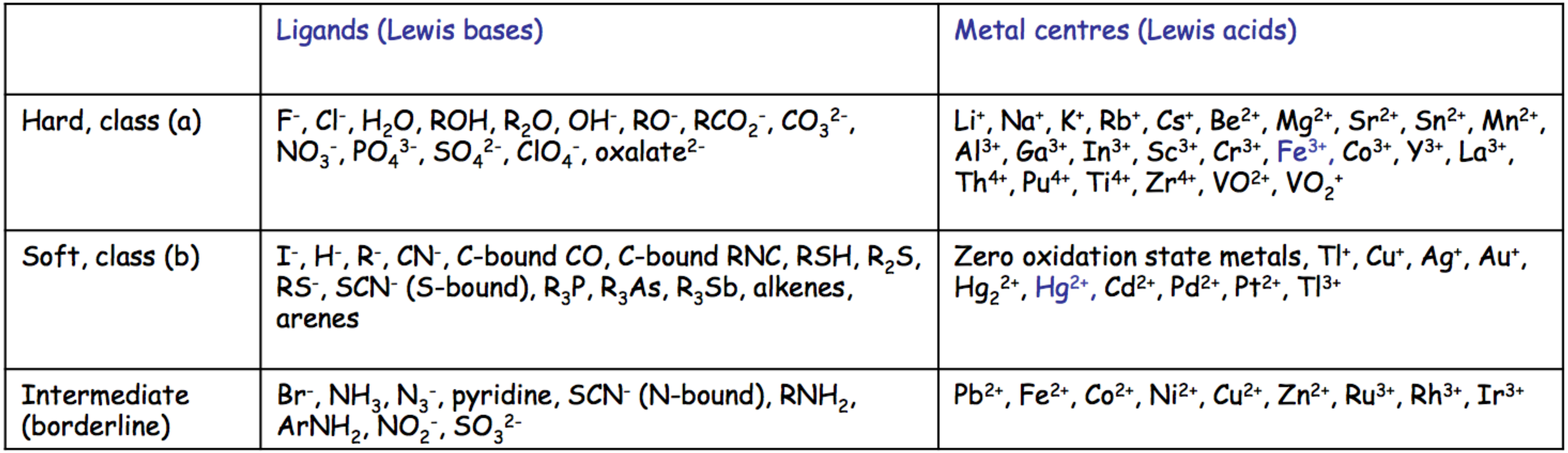
Order of increasing stability in complexes for **Hard** metal ions: O >> S > Se > Te
N >> P > As > Sb

Order of increasing stability in complexes for **Soft** metal ions: O << S > Se ~ Te
N << P > As > Sb

Order of decreasing hardness based on electronegativity:
F > O > N > Cl > Br > C ~ I ~ S > Se > P > As > Sb

Housecroft and Sharpe, Chapter 7, page 207

Thermodynamics of metal complex formation
HSAB Theory



	Ligands (Lewis bases)	Metal centres (Lewis acids)
Hard, class (a)	F^-, Cl^-, H_2O, ROH, R_2O, OH^-, RO^-, RCO_2^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-, oxalate^{2-}	Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Sr^{2+}, Sn^{2+}, Mn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, La^{3+}, Th^{4+}, Pu^{4+}, Ti^{4+}, Zr^{4+}, VO^{2+}, VO_2^+
Soft, class (b)	I^-, H^-, R^-, CN^-, C-bound CO, C-bound RNC, RSH, R_2S, RS^-, SCN^- (S-bound), R_3P, R_3As, R_3Sb, alkenes, arenes	Zero oxidation state metals, Tl^+, Cu^+, Ag^+, Au^+, Hg_2^{2+}, Hg^{2+}, Cd^{2+}, Pd^{2+}, Pt^{2+}, Tl^{3+}
Intermediate (borderline)	Br^-, NH_3, N_3^-, pyridine, SCN^- (N-bound), RNH_2, $ArNH_2$, NO_2^-, SO_3^{2-}	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}

Order of increasing stability in complexes for **Hard** metal ions: $O \gg S > Se > Te$
$N \gg P > As > Sb$

Order of increasing stability in complexes for **Soft** metal ions: $O \ll S > Se \sim Te$
$N \ll P > As > Sb$

Order of decreasing hardness based on electronegativity:
$F > O > N > Cl > Br > C \sim I \sim S > Se > P > As > Sb$

Housecroft and Sharpe, Chapter 7, page 207

Thermodynamics of metal complex formation
HSAB Theory

Ligands displace water in a competitive process – not a simple combination

If the M^{n+} is a **hard** metal - it is already associated with **hard H_2O** ligands. Thus reaction with another hard ligand may not be favourable – only a small exothermic enthalpy effect might be seen.

Leads only to moderately stable complexes ($-\Delta G^o$ small)
e.g., with L = RCO_2^-, F^-, Cl^- etc.

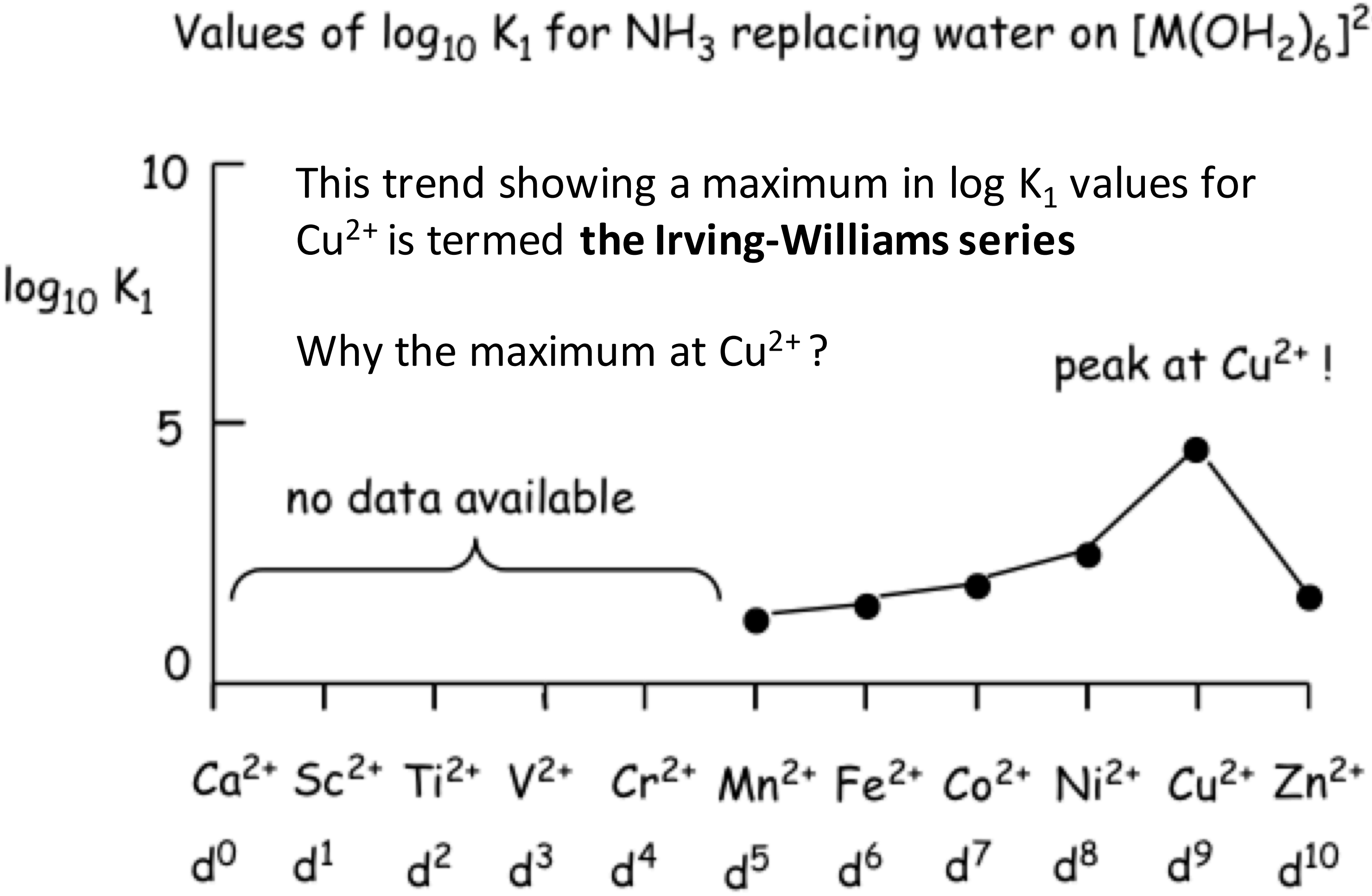
Now if M^{n+} is a **soft** metal and **L a soft base** the reaction is now highly favoured since it removes two unfavourable soft-hard interactions - from water solvation

Here a significant ΔH^o effect (large and negative) is seen when the soft-soft interaction results - leads to stable complexes with ΔG^o that is also large and negative (ΔS^o small as before) - high K_n
e.g., Hg^{2+}_{aq} and S^{2-}_{aq} ➞ HgS(s) precipitates

Thermodynamics of metal complex formation

We have examined the values of log K_n (β_n) for the successive replacement of H_2O on Ni^{2+}_{aq} by NH_3

What happens along the 3d series from Sc – Zn?



Values of $\log_{10} K_1$ for NH_3 replacing water on $[M(OH_2)_6]^{2+}$

This trend showing a maximum in log K_1 values for Cu^{2+} is termed **the Irving-Williams series**

Why the maximum at Cu^{2+}?

Electronic Structure and Properties of Complexes: Octahedral Complexes

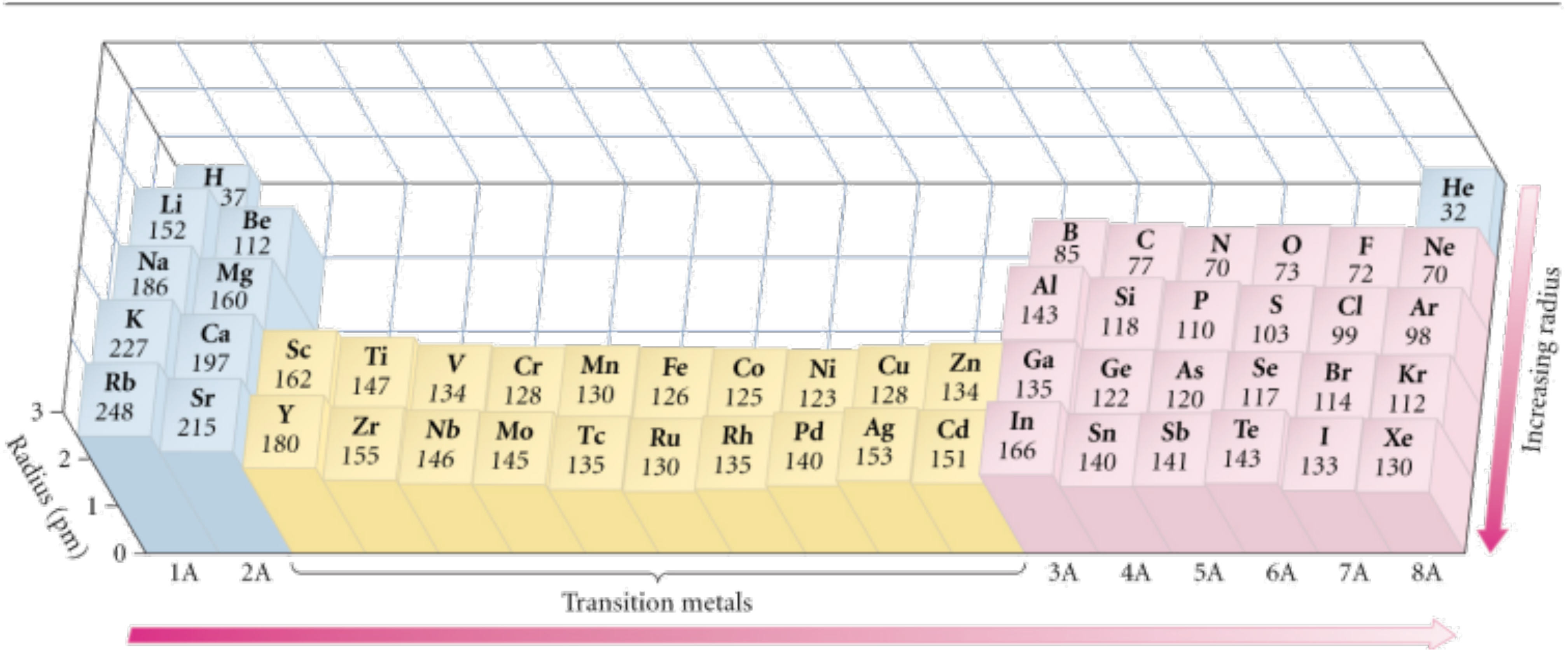
The Irving-Williams Series

The Irving-Williams Series (IWS) describes an empirical increase in stability of M^{2+} octahedral complexes as a function of atomic radius, regardless of the nature of L for the following reaction:

$$[M(H_2O)_n]^{2+} + L \rightleftharpoons [M(H_2O)_{n-1}L]^{2+} + H_2O$$

K_f varies along: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

Trends in Atomic Radius



Electronic Structure and Properties of Complexes: Octahedral Complexes
The Irving-Williams Series

The Irving-Williams Series (IWS) describes an empirical increase in stability of M^{2+} octahedral complexes as a function of atomic radius, regardless of the nature of L for the following reaction:

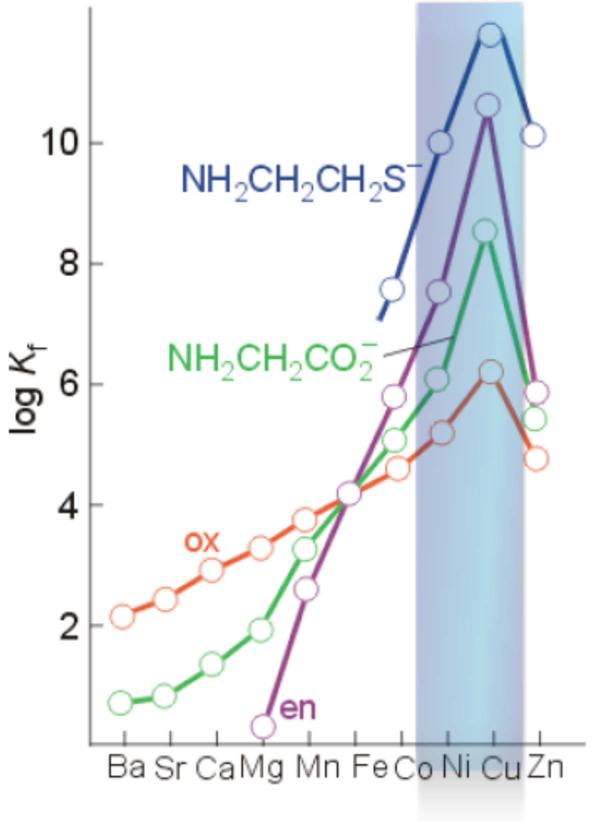
$$[M(H_2O)_n]^{2+} + L \rightleftharpoons [M(H_2O)_{n-1}L]^{2+} + H_2O$$

K_f varies along: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

reflects electrostatic effects
smaller metal with same charge = greater charge density

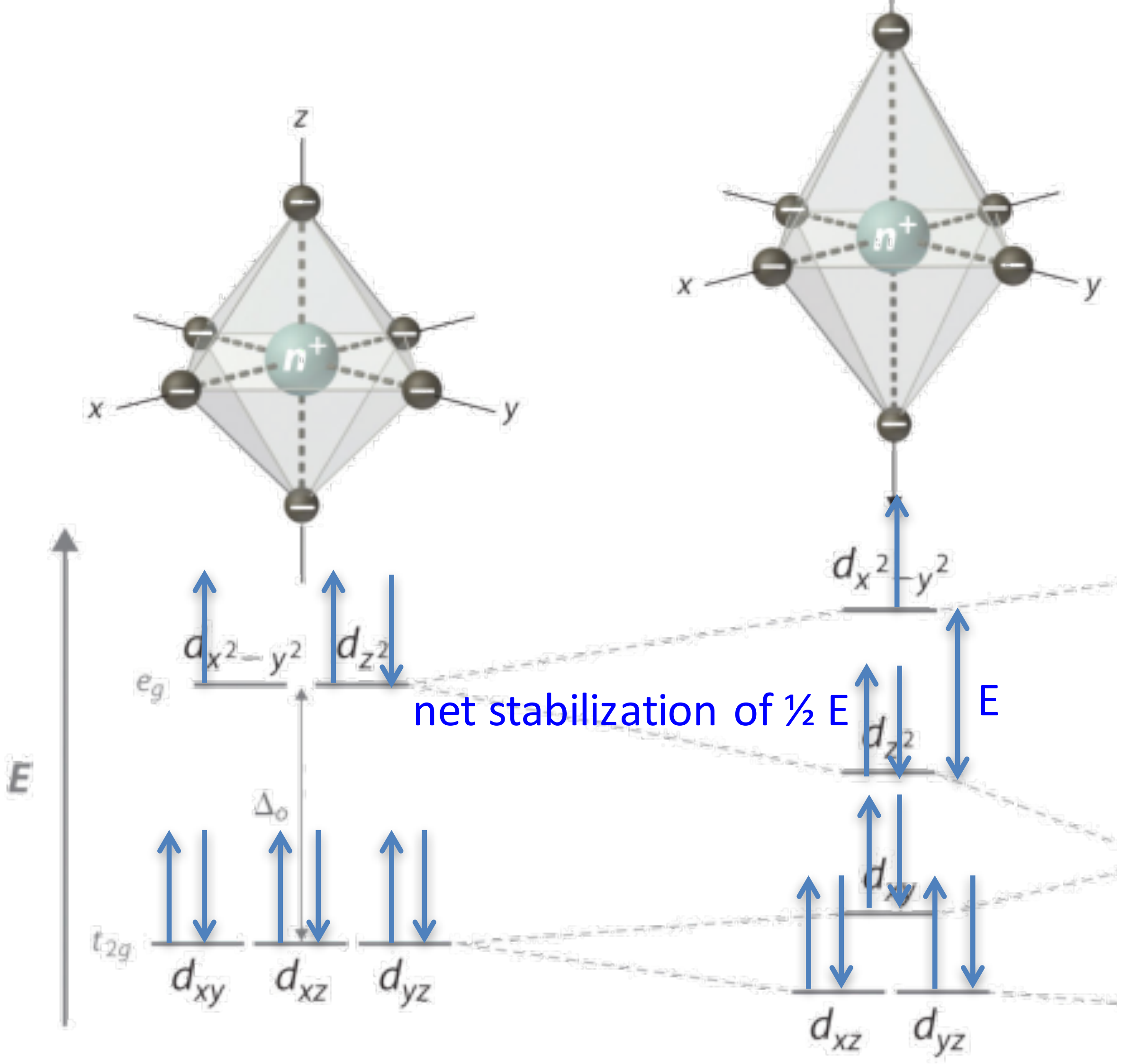
Based purely on electrostatics we would expect stabilities to vary as
$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Cu^{2+} > Zn^{2+}$

Exception: Cu^{2+} is actually more stable than Ni^{2+} and this is due to the Jahn Teller Distortion



Jahn-Teller Distortion – A Short Overview

Occurs when you can asymmetrically fill orbitals that are degenerate in a non-linear complex. The geometry of the complex then distorts to reach a more stable electronic configuration



High spin d^4 $t_{2g}^3e_g^1$
Low spin d^7 $t_{2g}^6e_g^1$ or d^9 $t_{2g}^6e_g^3$

Let’s look at the case for LS d^9 $t_{2g}^6e_g^3$

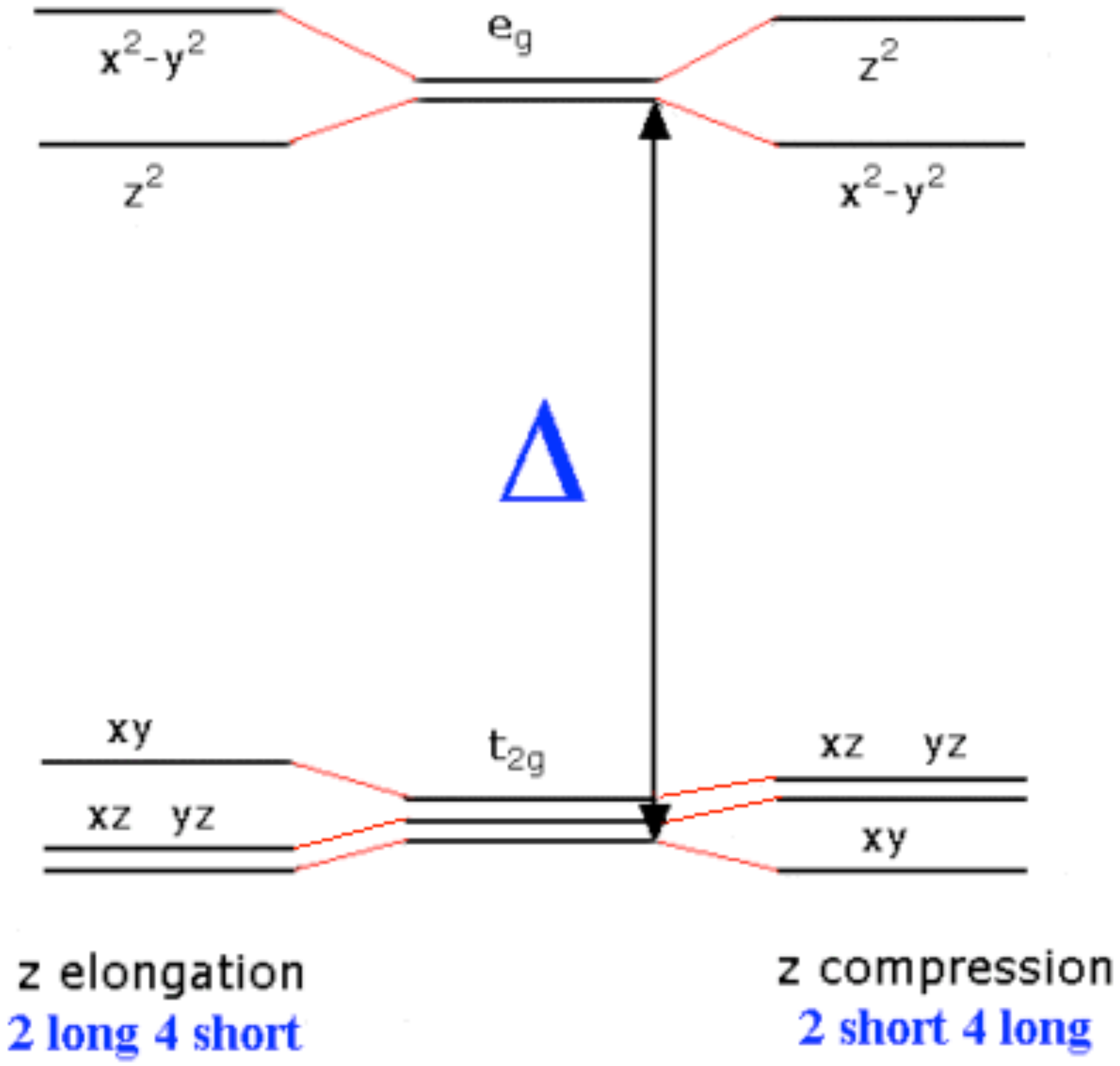
If there are 2e in d_{z2} and 1e in d_{x2-y2} then greater repulsion along the z-axis ∴ elongation of these M-L bonds along the z-axis to compensate, leading to stabilization of the d_{z2} orbital – *most common distortion*

University of St Andrews

CH3514

Jahn-Teller Distortion – A Short Overview

Occurs when you can asymmetrically fill orbitals that are degenerate in a non-linear complex. The geometry of the complex then distorts to reach a more stable electronic configuration



High spin d^4 $t_{2g}^3e_g^1$
Low spin d^7 $t_{2g}^6e_g^1$ or d^9 $t_{2g}^6e_g^3$

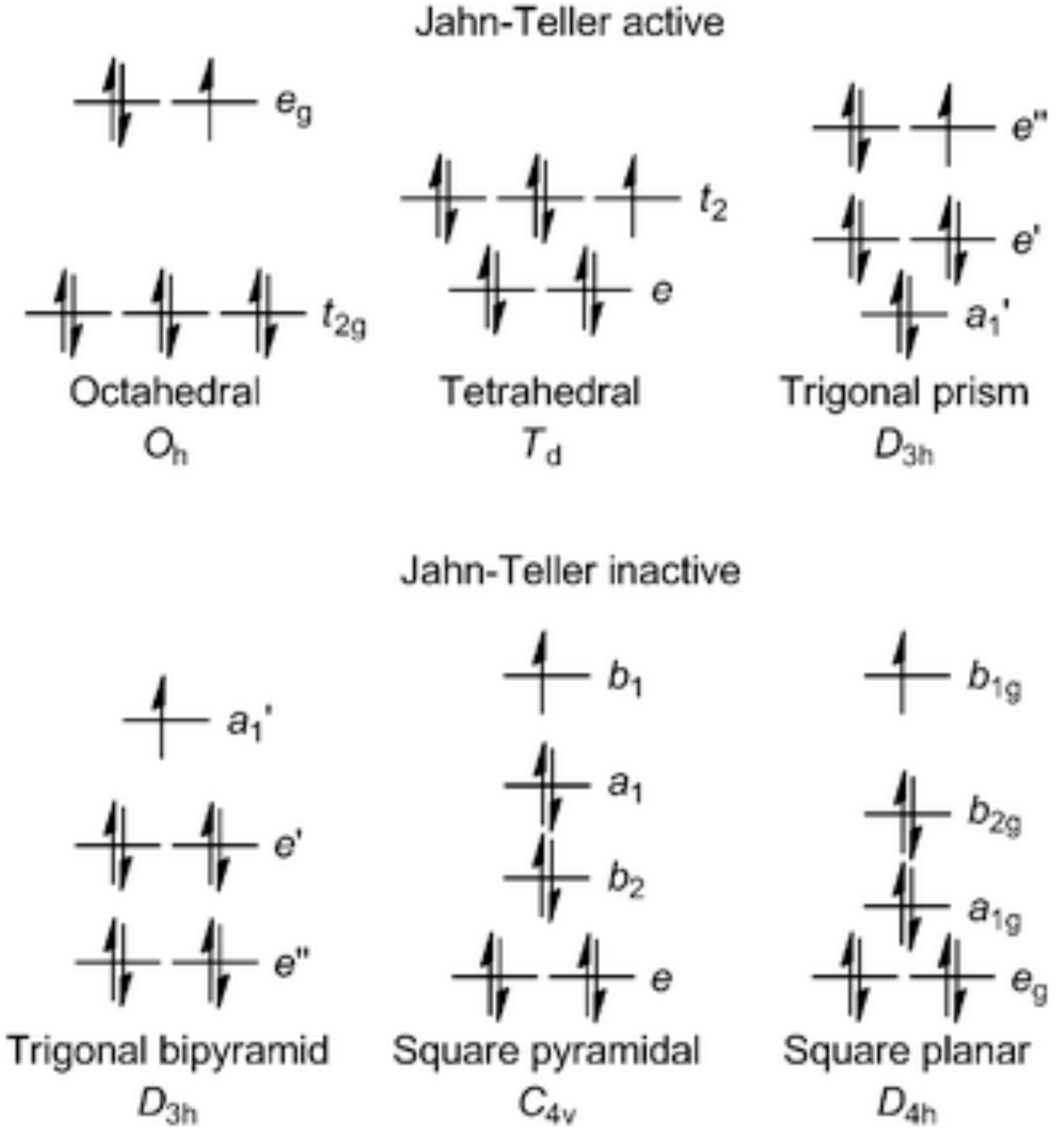
Let's look at the case for LS d^9 $t_{2g}^6e_g^3$

If there are 2e in d_{z2} and 1e in d_{x2-y2} then greater repulsion along the z-axis ∴ elongation of these M-L bonds along the z-axis to compensate, leading to stabilization of the d_{z2} orbital – *most common distortion*

If there are 2e in d_{x2-y2} and 1e in d_{z2} then greater repulsion along the xy-plane ∴ effective compression of the M-L bonds along the z-axis to compensate, leading to stabilization of the d_{x2-y2} orbital

Jahn-Teller Distortion – A Short Overview

Occurs when you can asymmetrically fill orbitals that are degenerate in a non-linear complex. The geometry of the complex then distorts to reach a more stable electronic configuration

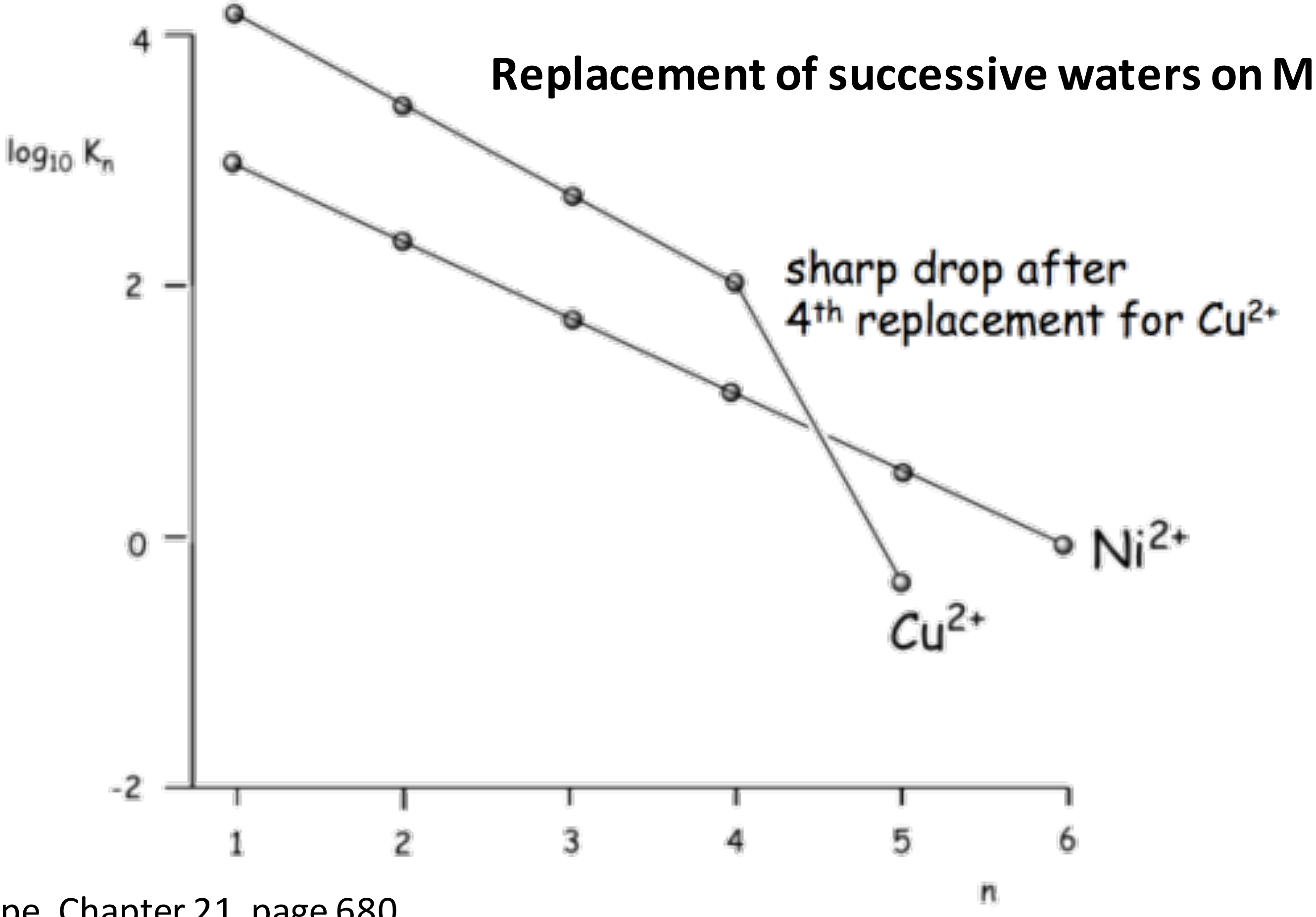


Thermodynamics of metal complex formation
The Impact of Jahn-Teller Distortion

The presence of only **one electron** in the d_{x2-y2} orbital strengthens the water ligand attraction in the equatorial plane due to lower e-e repulsion with the donor O electrons

The result is a raising in log K_{1-4} and a lowering in log K_5 and K_6 for water substitution compared to the two ions either side; Ni^{2+} (d^8) and Zn^{2+} (d^{10}) where there is no such extra stabilization

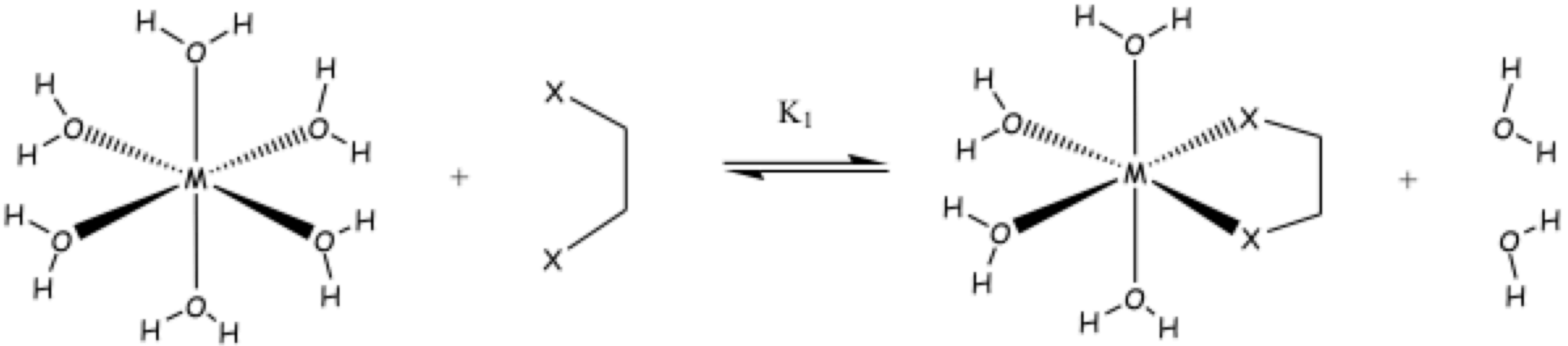
Replacement of successive waters on M^{2+}_{aq} by NH_3

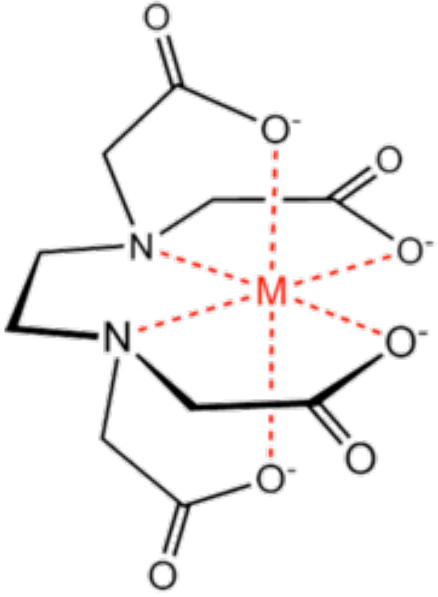


Housecroft and Sharpe, Chapter 21, page 680

Thermodynamics of metal complex formation
The Chelate Effect

Let’s now consider the situation when the ligand L replacing coordinated water possesses two donor atoms that lead to the formation of a **chelate** ring





EDTA complex with Cu^{2+}

Thermodynamics of metal complex formation
The Chelate Effect

Let’s now consider the situation when the ligand L replacing coordinated water possesses two donor atoms that lead to the formation of a **chelate** ring

The figure shows that the replacement of NH_3 on M^{2+}_{aq} by the chelates en and EDTA is thermodynamically favourable.

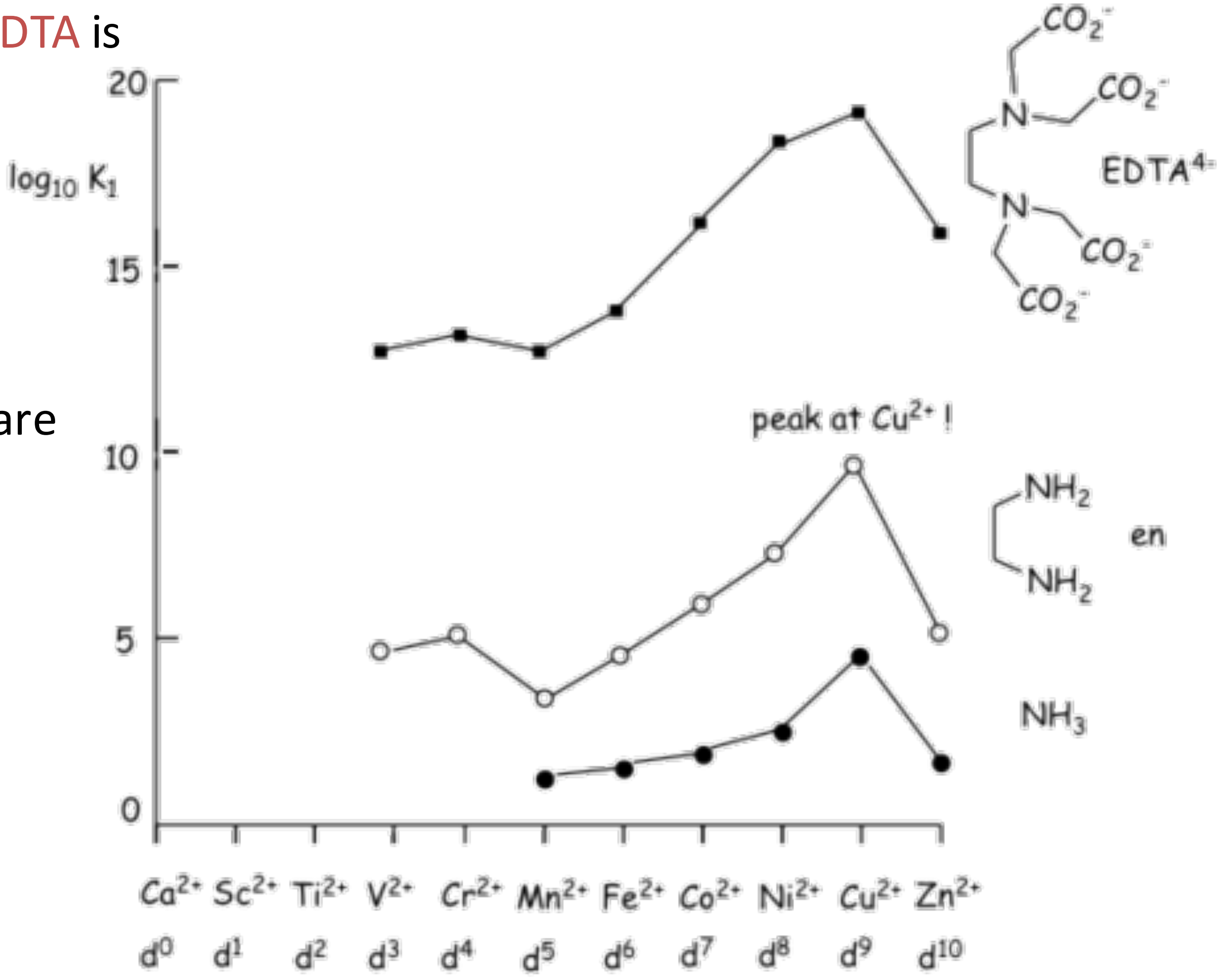
This is a general phenomenon called the **chelate effect**

The increase in log K_1 as chelate rings are formed is a reflection of a more negative value of ΔG^o_1

It is largely due to an **increase in the entropy** of reaction
i.e. ΔS^o_1 is large and positive

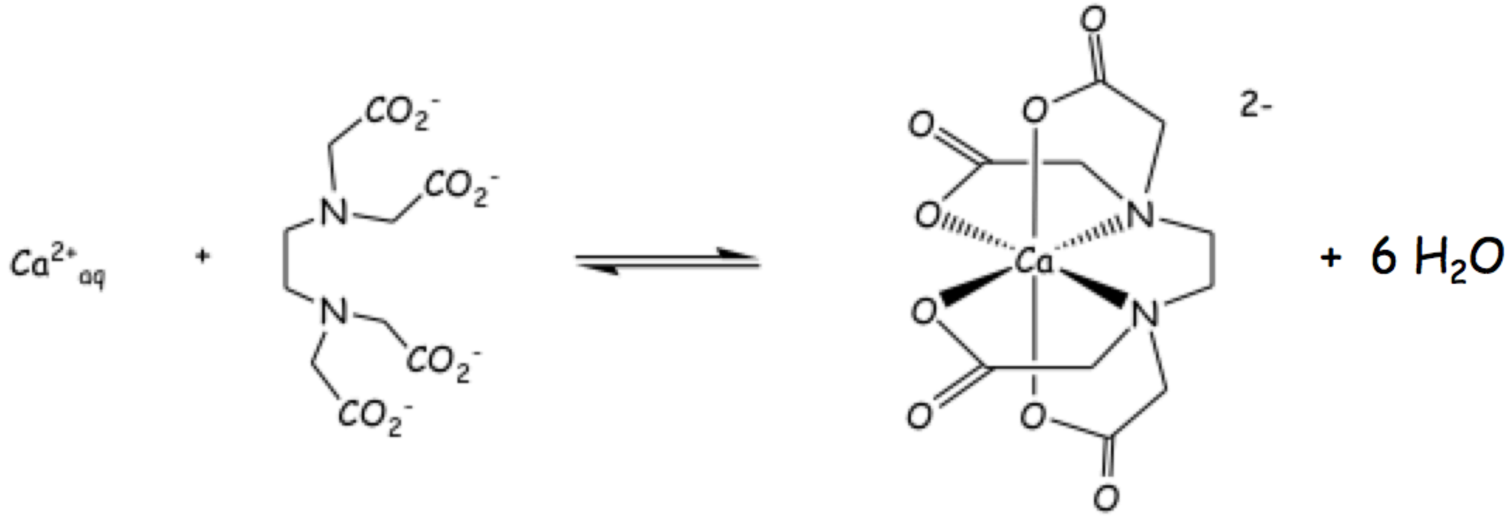
$\Delta G^o_1 = \Delta H^o_1 - T\Delta S^o_1$

Values of $\log_{10} K_1$ for various L replacing water on $[M(OH_2)_6]^{2+}$



Thermodynamics of metal complex formation
The Chelate Effect

Let’s look at a specific example: Ca^{2+}_{aq} + $EDTA^{4-}$



ΔG^o_1 = -60.5 KJ mol^{-1}; ΔS^o_1 = 117 J mol^{-1} K^{-1}

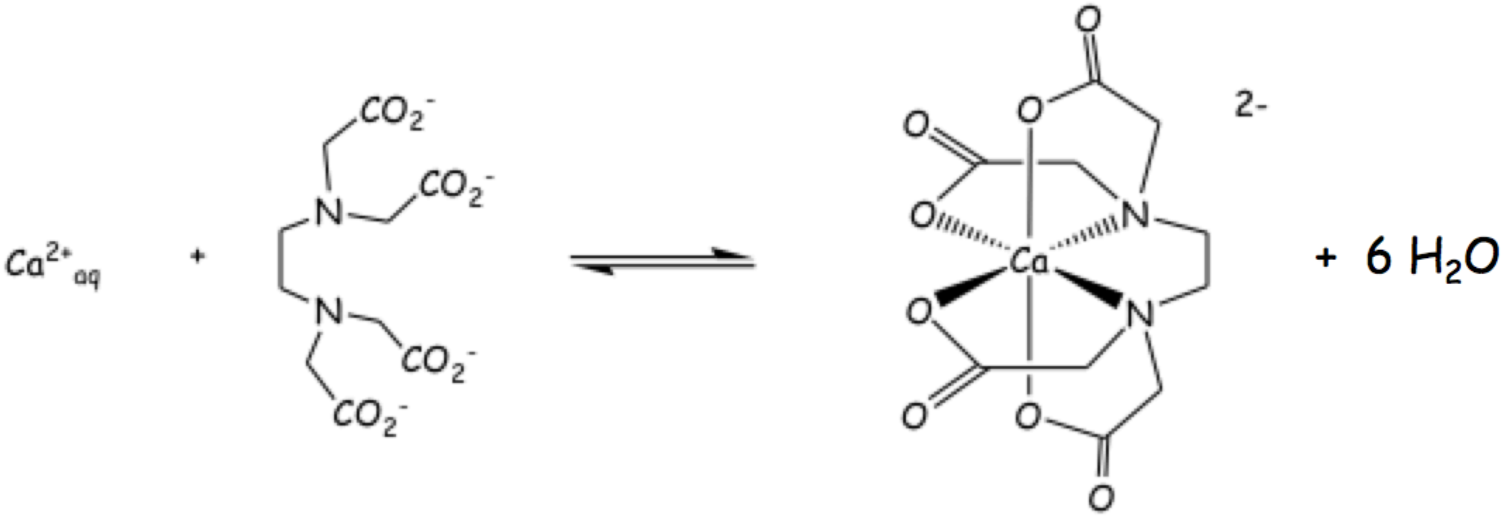
At 300 K, ΔH^o_1 = -25.4 KJ mol^{-1} ($\Delta H^o_1 = \Delta G^o_1 + T\Delta S^o_1$)

Therefore this complexation is mostly entropy driven ($T\Delta S^o_1$ = -35.1 KJ mol^{-1})
Though there is a favourable enthalpic term as well (HSAB and chelate effect).

Why entropy controlled? There is an increase in entropy due to release of 6 water molecules – increase in disorder of the system

Thermodynamics of metal complex formation
The Chelate Effect

Let’s look at a specific example: Ca^{2+}_{aq} + $EDTA^{4-}$



ΔG^o_1 = -60.5 KJ mol^{-1}; ΔS^o_1 = 117 J mol^{-1} K^{-1}

At 300 K, ΔH^o_1 = -25.4 KJ mol^{-1} ($\Delta H^o_1 = \Delta G^o_1 + T\Delta S^o_1$)

We can now calculate K_1 as $\Delta G^o_1 = -RT \ln (K_1)$

$\log(K_1) = \log (e^{-\Delta G1/RT}) = 10.53$

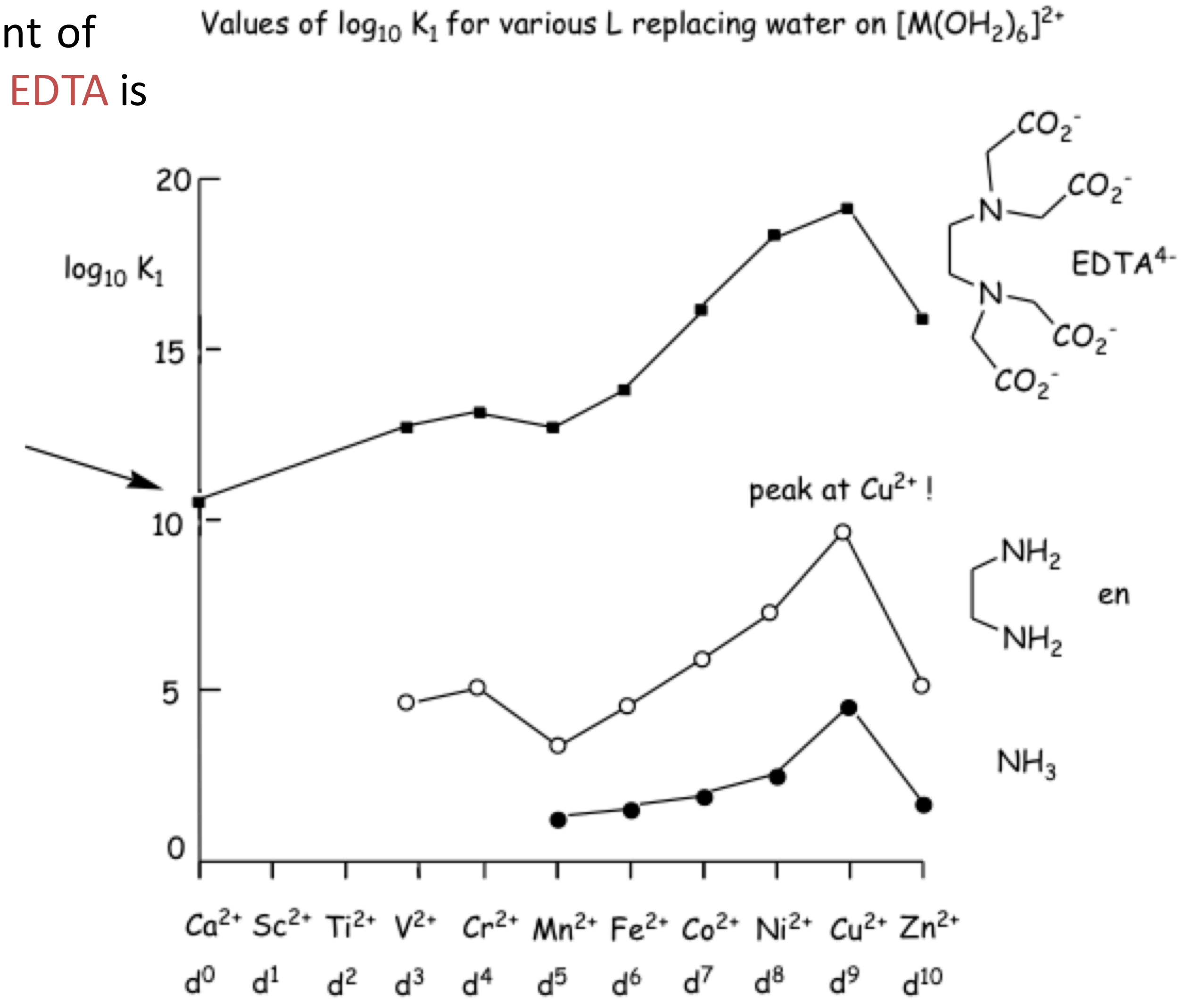
We can now add this point to the previous figure!

Thermodynamics of metal complex formation
The Chelate Effect

Let's look at a specific example: Ca^{2+}_{aq} + $EDTA^{4-}$

The figure shows that the replacement of NH_3 on M^{2+}_{aq} by the chelates en and EDTA is thermodynamically favourable.

This is a general phenomenon called the **chelate effect**


Values of $\log_{10} K_1$ for various L replacing water on $[M(OH_2)_6]^{2+}$

Thermodynamics of metal complex formation
The Chelate Effect

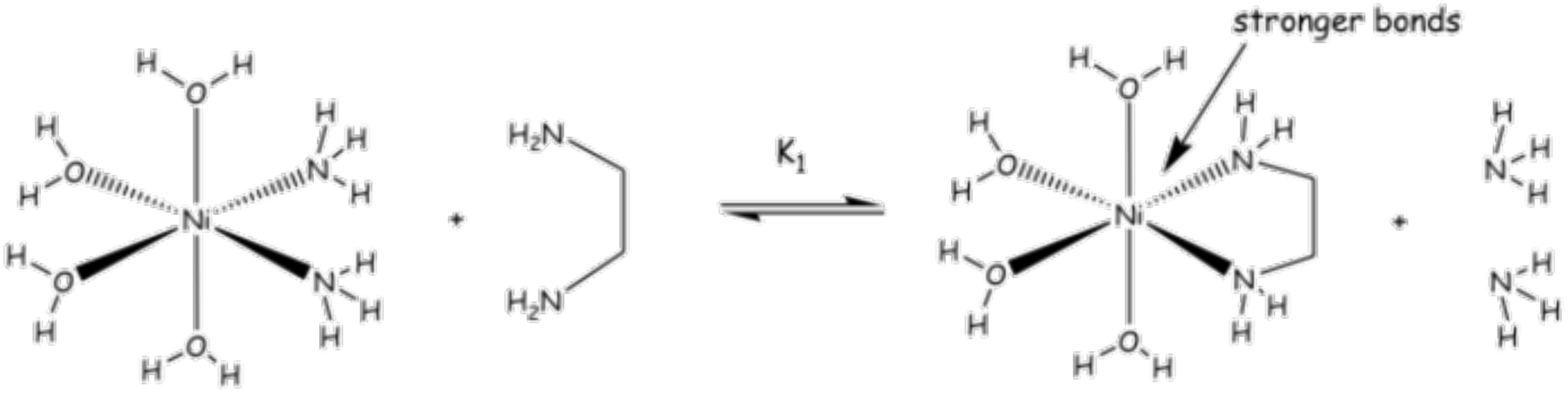
Let’s look at another specific example: $[Ni(NH_3)_6]^{2+} + 3$ en

$$\underbrace{[Ni(NH_3)_6]^{2+} + 3\,en}_{4\ species} \xrightleftharpoons{\beta_3} \underbrace{[Ni(en)_3]^{2+} + 6\,NH_3}_{7\ species}$$

$\mathbf{\Delta G^o_1} = -57.2$ KJ mol^{-1}; $\mathbf{\Delta H^o_1} = -16.6$ KJ mol^{-1}; $\mathbf{-T\Delta S^o_1} = -36.1$ KJ mol^{-1}

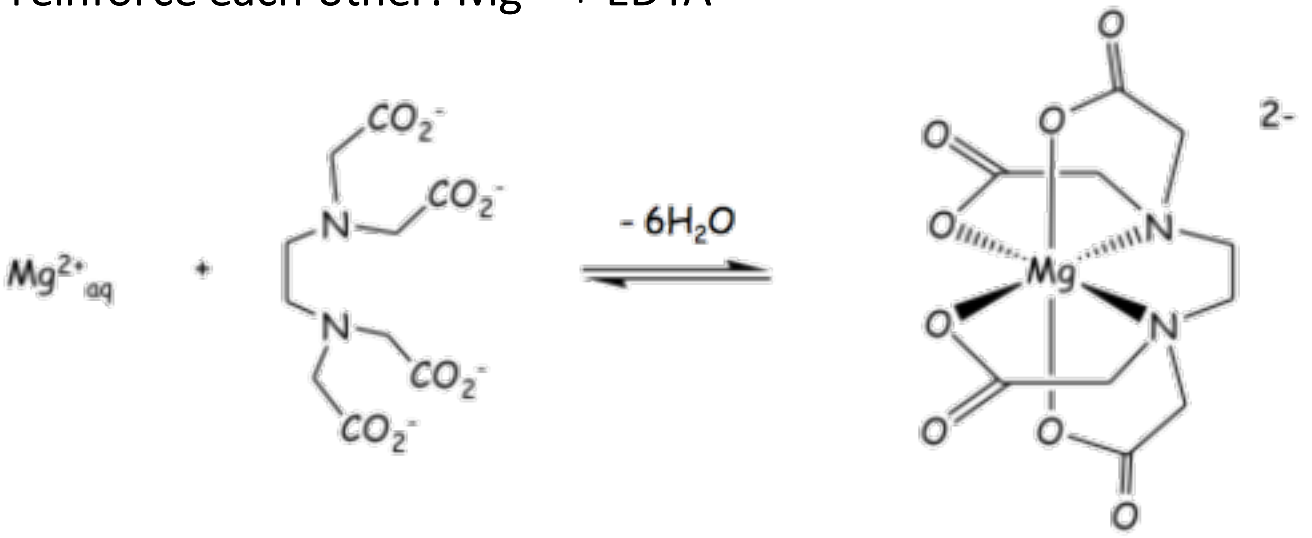
both enthalpy and entropy effects reinforce

The **enthalpic effect** on chelation from **en** arises from stronger bonds to the **N** donors of the chelate as a result of the formation of the ring



Thermodynamics of metal complex formation
The Chelate Effect

Let’s look at another specific example where the enthalpy and entropy terms **do not** reinforce each other: Mg^{2+} + $EDTA^{4-}$



$\Delta G^o_1 = -51.2$ KJ mol^{-1}; $\Delta H^o_1 = 13.8$ KJ mol^{-1}; $-T\Delta S^o_1 = -65.0$ KJ mol^{-1}

Here the endothermic enthalpy term arises from the unfavourable replacement of two hard water ligands on the extremely hard Mg^{2+} by the softer N donors of $EDTA^{4-}$ (HSAB).

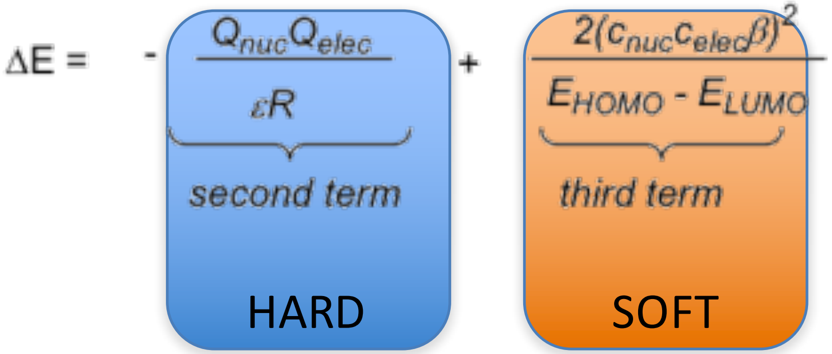
Formation of the chelate is however still highly favoured due to the favourable entropy contribution

Thermodynamics of metal complex formation
The Chelate Effect

This begs the question why is Mg^{2+} harder than Ca^{2+}?

Mg^{2+} is smaller (charge more concentrated) than Ca^{2+}, which will reinforce the electrostatic interaction (Hard-Hard) interaction with H_2O

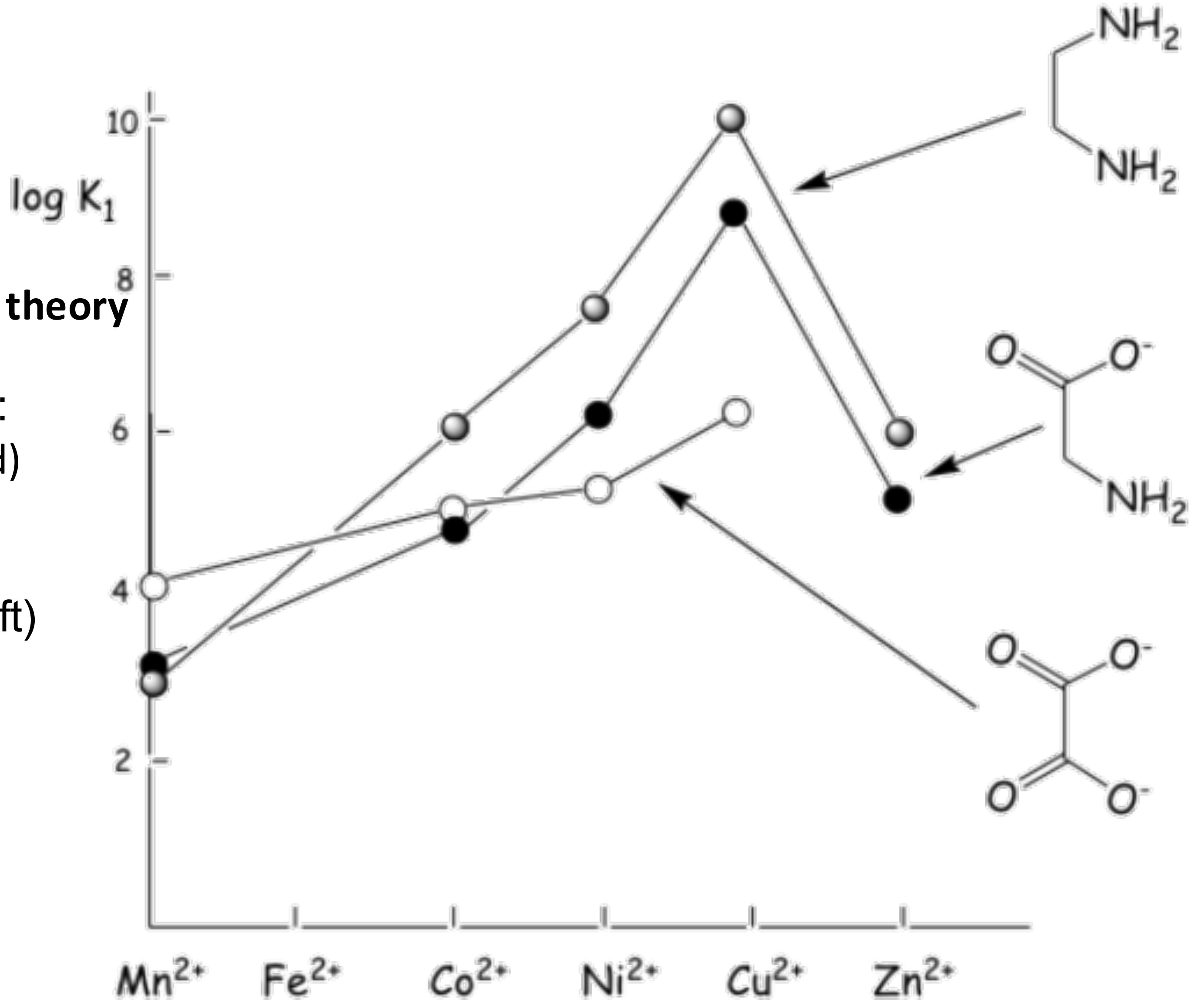
Salem-Klopman Equation (simplified)



$$\Delta E = -\underbrace{\frac{Q_{nuc}Q_{elec}}{\varepsilon R}}_{\text{second term}} + \underbrace{\frac{2(c_{nuc}c_{elec}\beta)^2}{E_{HOMO} - E_{LUMO}}}_{\text{third term}}$$

Thermodynamics of metal complex formation
The Chelate Effect

We can also probe the effect of the nature of the donor atom on the binding strength to the metal.



Order of log K_1 reflects HSAB theory

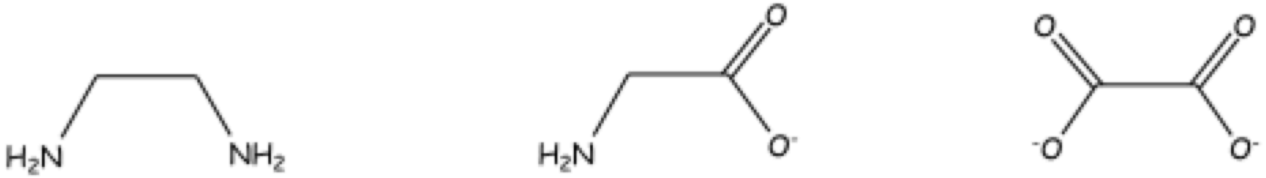
For Ni^{2+} to Zn^{2+} (soft metals):
(soft) N^N > N^O > O^O (hard)

For Mn^{2+} (hard metal):
(hard) O^O > N^O > N^N (soft)

Thermodynamics of metal complex formation
The Chelate Effect

We can also probe the effect of the nature of the donor atom on the binding strength to the metal.

M^{2+}_{aq}



increasing hardness →

increasing softness ↓

T = 300K	ΔH^o_1 kJ mol^{-1}	$-T\Delta S^o_1$ kJ mol^{-1}	ΔH^o_1 kJ mol^{-1}	$-T\Delta S^o_1$ kJ mol^{-1}	ΔH^o_1 kJ mol^{-1}	$-T\Delta S^o_1$ kJ mol^{-1}
Mn	-11.7	-3.8	-1.3	-16.9	+15.4	-34.2
Fe	-21.3	-6.4	-	-	-	-
Co	-28.9	-8.7	-11.7	-17.2	+12.1	-33.9
Ni	-37.2	-10.8	-20.5	-14.9	+7.9	-31.5
Cu	-54.4	-16.3	-25.9	-23.1	+11.9	-44.4
Zn	-28.0	-8.4	-13.8	-15.9	+13.1	-35.1

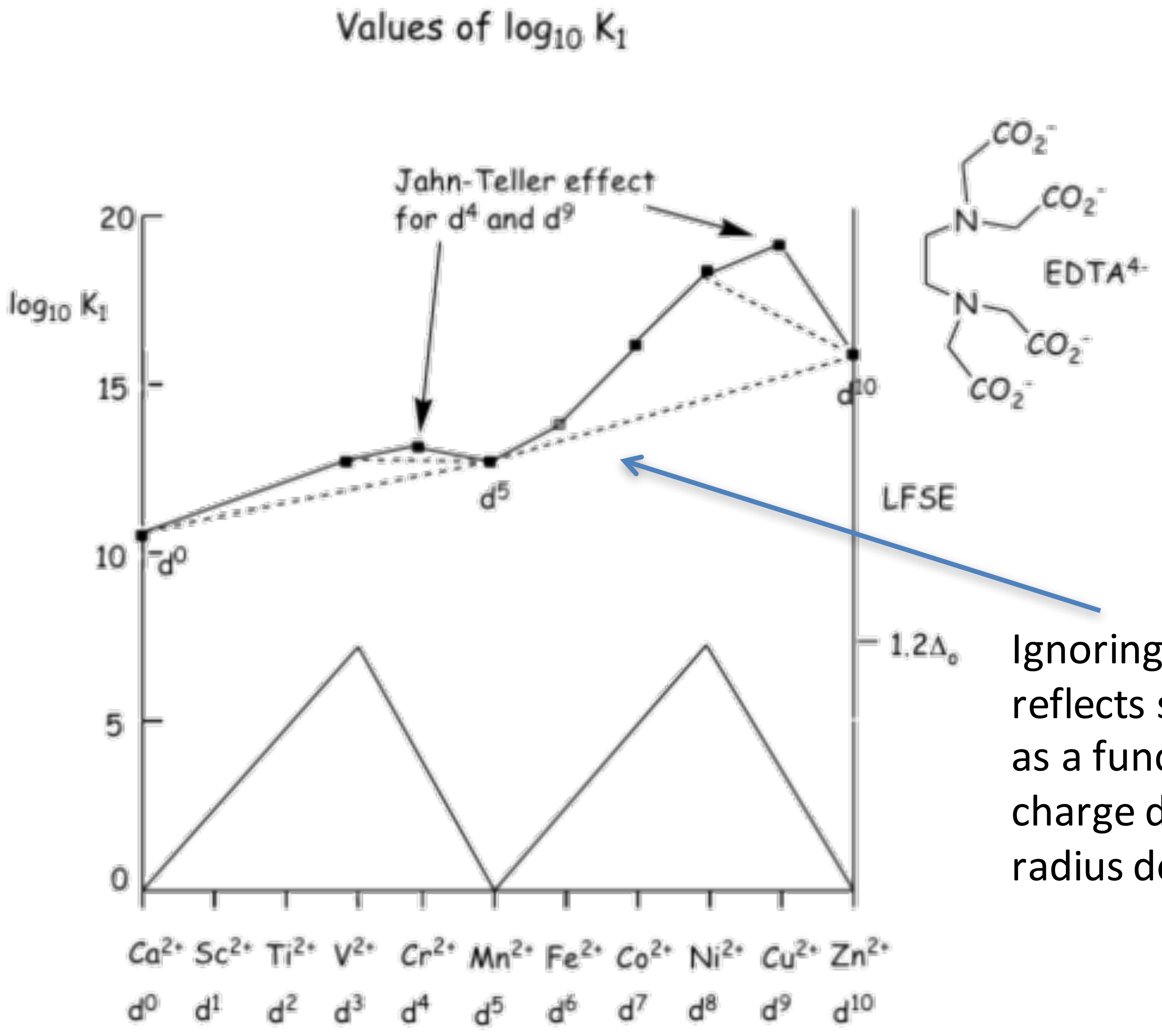
ΔH^o and $-T\Delta S^o$ terms reinforce

ΔH^o and $-T\Delta S^o$ terms reinforce

complexation is entropy favoured only

Thermodynamics of metal complex formation
The Chelate Effect

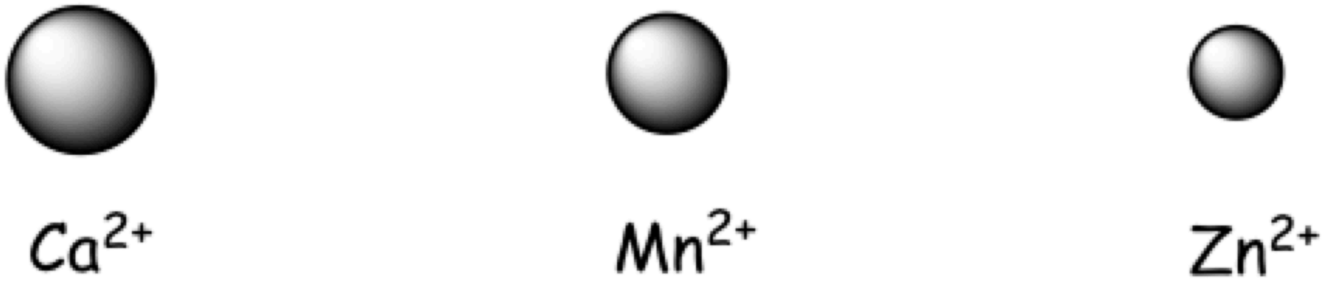
Binding strength is also influenced by the number of d electrons on the metal (LFSE)



Ignoring LFSE, increasing K_1 reflects stronger M-L bonding as a function of increasing charge density on the M as the ionic radius decreases along the period

Thermodynamics of metal complex formation
The Chelate Effect

Why does the ionic radius decrease along the period?



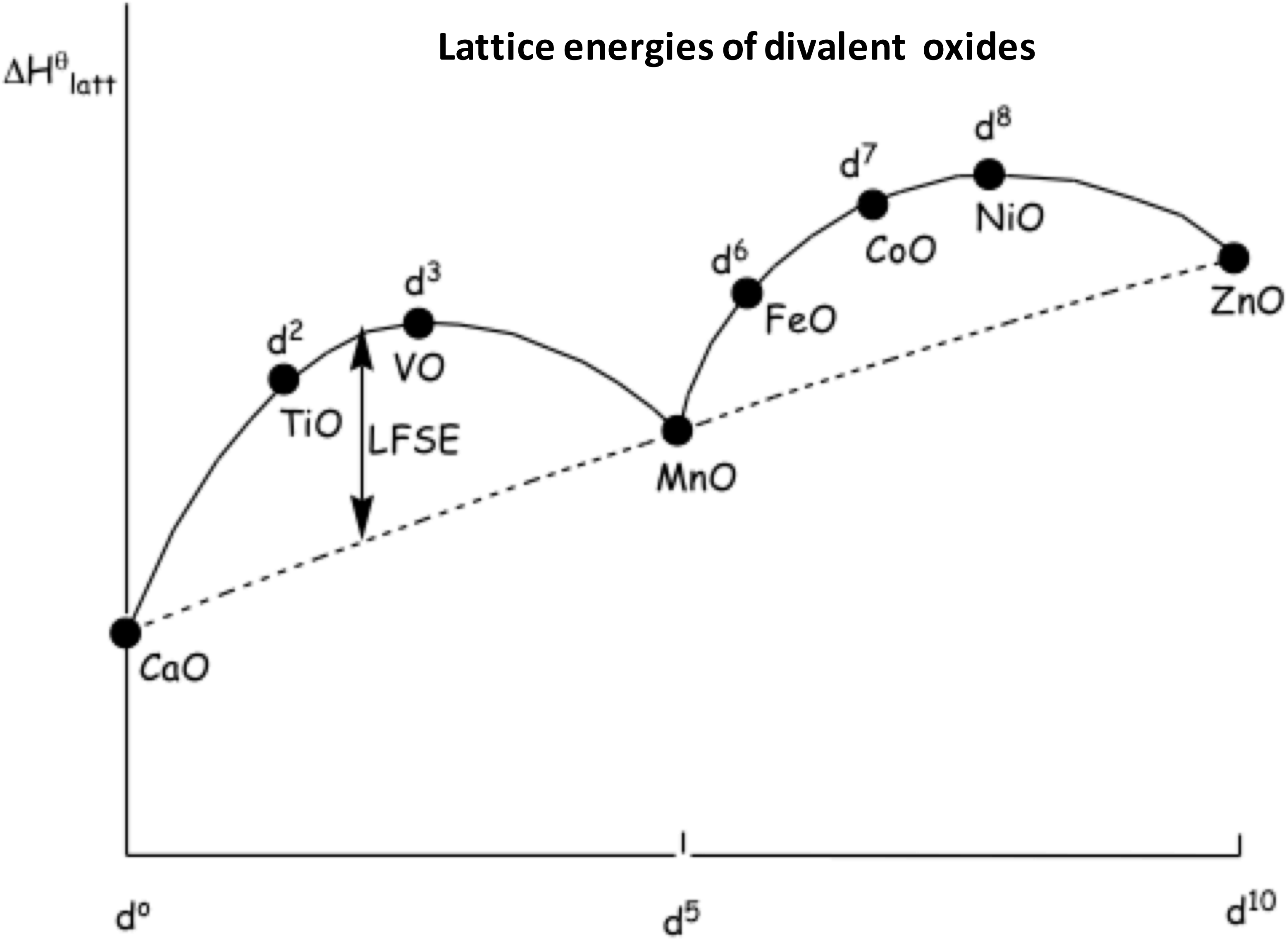
The decreasing metal ion radius along the period is a result of the poor shielding of the nuclear charge by the addition of the successive d–electrons

The d-orbitals do not penetrate into the nucleus because the d orbital wave function goes to zero before the nucleus is reached

Thermodynamics of metal complex formation
The Chelate Effect

The same phenomenon is seen in other properties of 3d-metal complexes

Lattice energies of divalent oxides

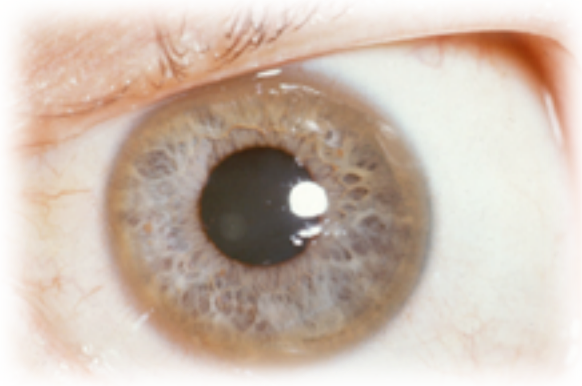


Chelate Ring Formation in Applications

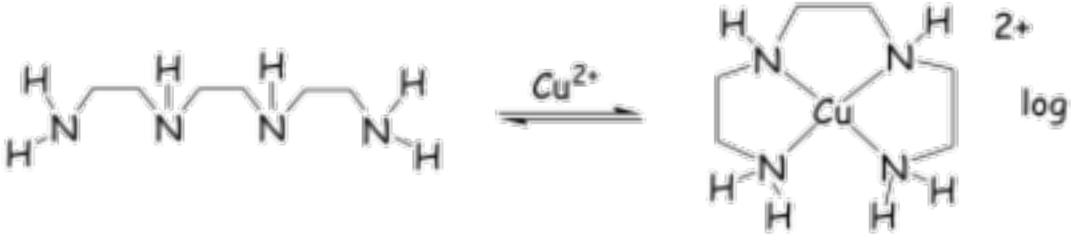
Chelation therapy has been used to treat diseases and conditions relating to metal overload

Wilson's disease is a recessive genetic disorder that causes epilepsy amongst other neurological symptoms and is due to an overload of copper

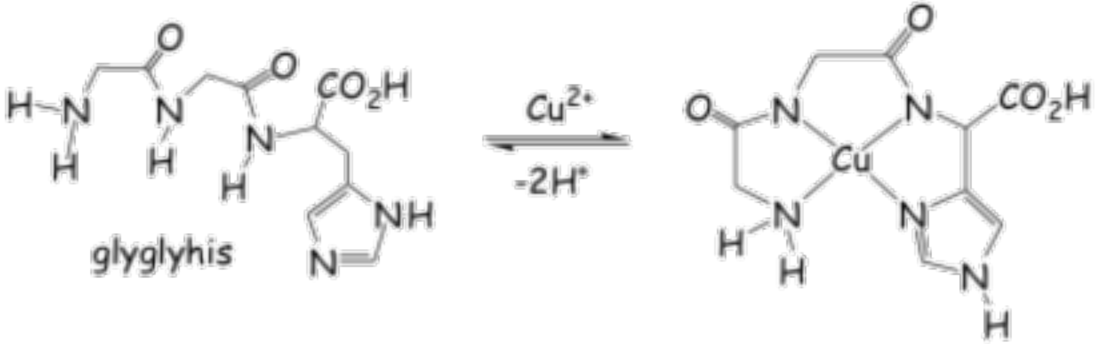
Chelating agents such as those below that bind Cu^{2+} ions strongly have been successfully used clinically to treat the condition



A Kayser-Fleischer ring



$\log K_1 = 20$ (highest amongst the 3d metals)

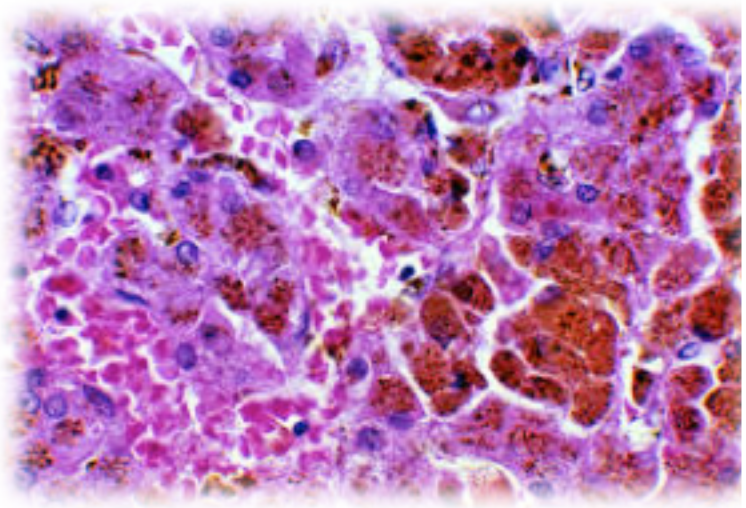


Chelate Ring Formation in Applications

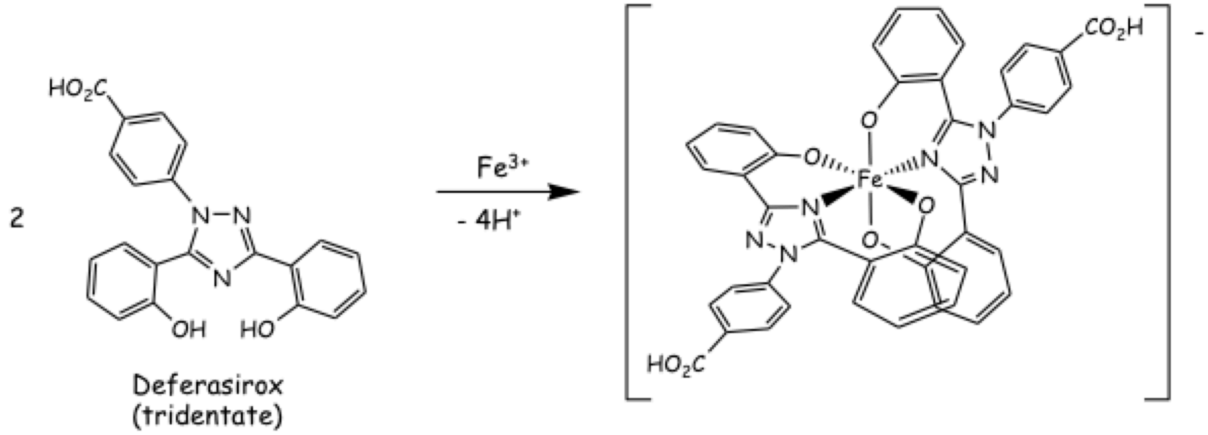
Chelation therapy has been used to treat diseases and conditions relating to metal overload

A potentially fatal condition called **hemosiderosis** occurs when the naturally occurring iron carrier protein **transferrin** becomes saturated and iron becomes deposited within the body.

In cases of severe iron overload, deposition in the heart, liver and endocrine systems leads to functional impairment of these organs, and reduced life expectancy.



Hemosiderosis of the liver



Deferasirox (tridentate)

manufactured as 'Exjade' by Novartis

US FDA approved – Nov 2005

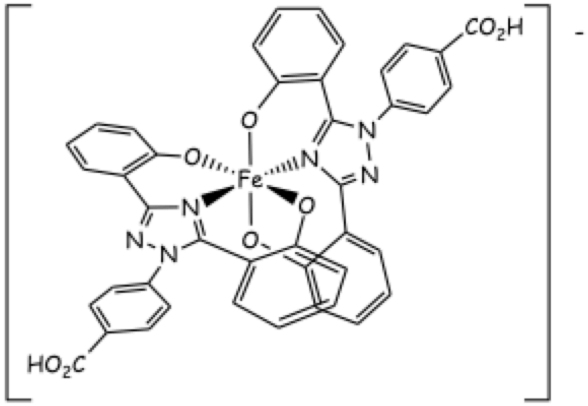
excreted

Chelate Ring Formation in Applications

Chelation therapy has been used to treat diseases and conditions relating to metal overload

A potentially fatal condition called **hemosiderosis** occurs when the naturally occurring iron carrier protein **transferrin** becomes saturated and iron becomes deposited within the body.

In cases of severe iron overload, deposition in the heart, liver and endocrine systems leads to functional impairment of these organs, and reduced life expectancy.

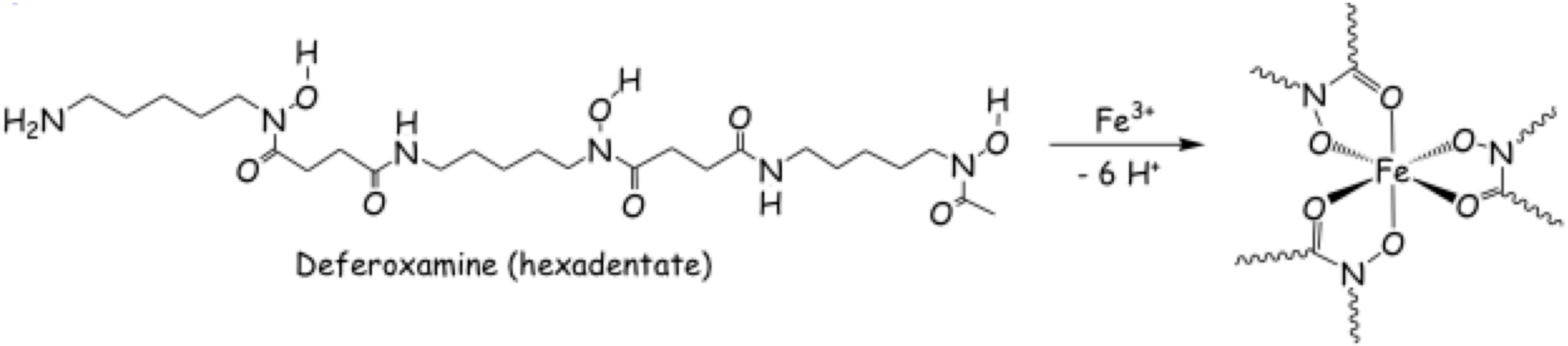


excreted

Chelate Ring Formation in Applications

Chelation therapy has been used to treat diseases and conditions relating to metal overload

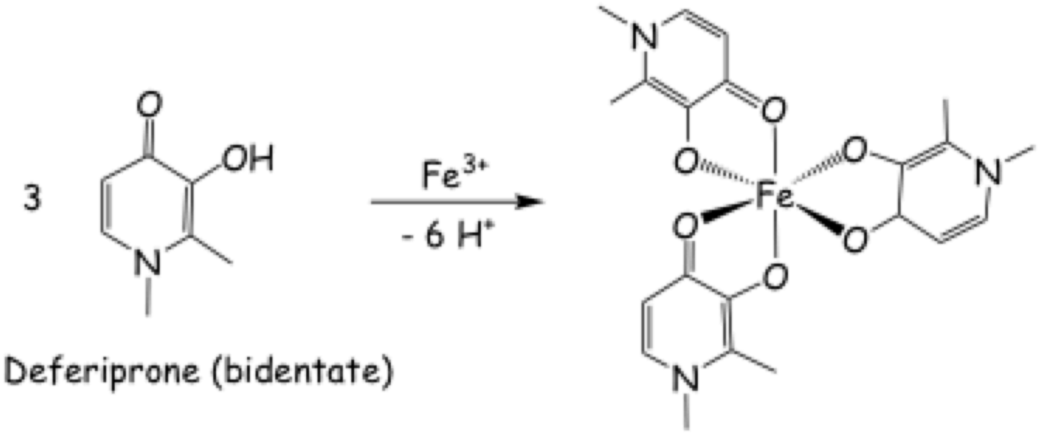
There exists other clinically proven agents for the removal of Fe^{3+} from the body



Deferoxamine (hexadentate)

binds through deprotonated hydroxamate groups

Note the affinity of the hard Fe^{3+} for hard **O** donors

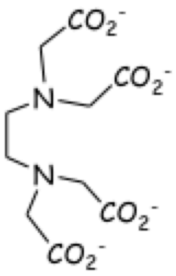


Deferiprone (bidentate)

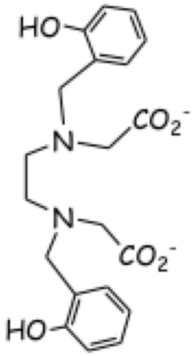
Chelate Ring Formation in Applications

Chelation therapy has been used to treat diseases and conditions relating to metal overload

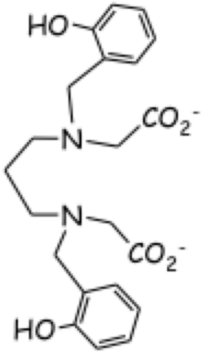
There exists other clinically proven agents for the removal of Fe^{3+} from the body



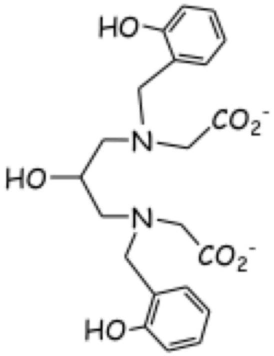
EDTA^{4-}



HBED^{2-}

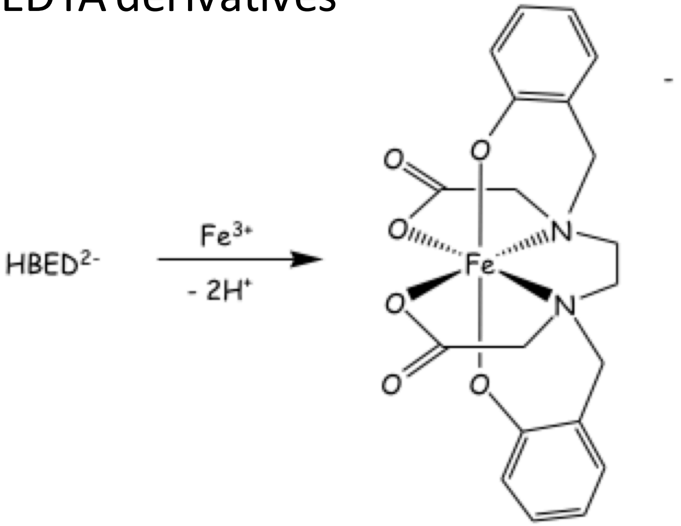


HBPD^{2-}



HBHPD^{2-}

These are all agents based on EDTA derivatives



US Patent 4528196

Stabilities of Oxidation States

The higher states become more oxidising and the lower states less reducing to the right

Why?

Due to the poor shielding of the nucleus by the addition of successive d-electrons, the effective positive charge felt by an outer electron increases from left to right.

This has two consequences:

- Decrease in ionic radius to the right.
- Valence electrons become harder to lose/share the more to the right you go.

– the higher oxidation states become more oxidizing and the lower states less reducing

Stabilities of Oxidation States

But how do we truly define the term **“oxidation state”**?

In nomenclature terms this is done by assuming octet configurations to define the charge on the atoms attached to the metal in the ion or complex

Complex	Ligand	Total Charge on Ligand	Overall Charge on Complex	Oxidation State of Metal
$[Mn(OH_2)_6]^{2+}$	H_2O	0	+2	II
MnO_4^-	O^{2-}	8-	-1	VII
$[Fe(CN)_6]^{4-}$	CN^-	6-	-4	II
$[Co(NH_3)_4(O_2CR)Cl]^+$	NH_3 RCO_2^- Cl^-	0 1- 1-	+1	III

In reality, oxidation states are a formalism and are only true if the M-L bonding is highly ionic (electrostatic).

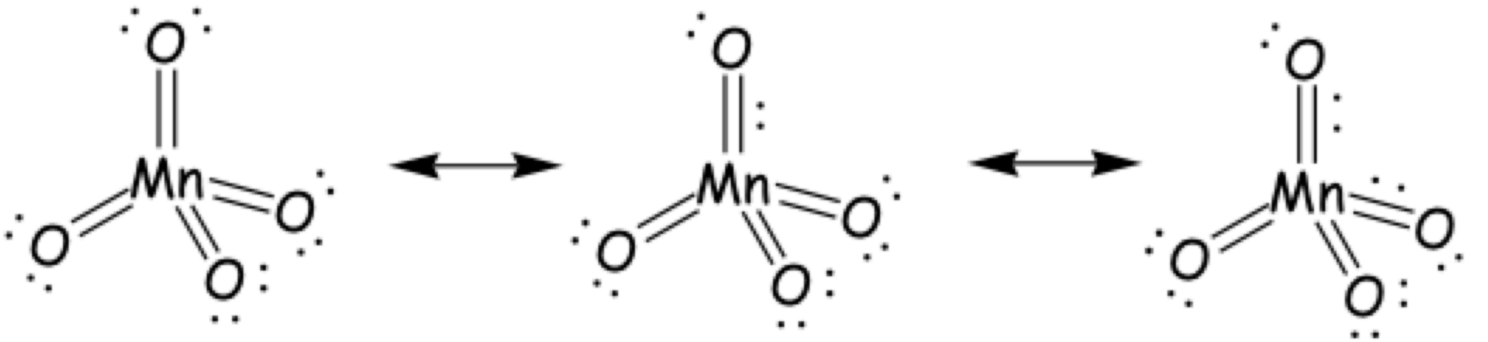
e.g., $[Mn(OH_2)_6]^{2+}$ where Mn is truly is Mn^{2+}

(independent evidence exists from optical spectroscopy and magnetism that it is high spin d^5)

Stabilities of Oxidation States

But what about the case of MnO_4^- where the Mn-O bonds are highly covalent (Mn-O bond length is less than sum of ionic radii)

So where now are the electrons?



$Mn^{7+}(O^{2-})_4$ $Mn^{6+}(O^{2-})_3\,(O^{-}\cdot)$ $Mn^{5+}(O^{2-})_2\,(O^{-}\cdot)_2$

Here optical spectroscopy and magnetism are less informative:

- spectra is dominated by O→Mn charge transfer bands
- it is diamagnetic

So we write as $Mn^{VII}(O^{-II})_4$

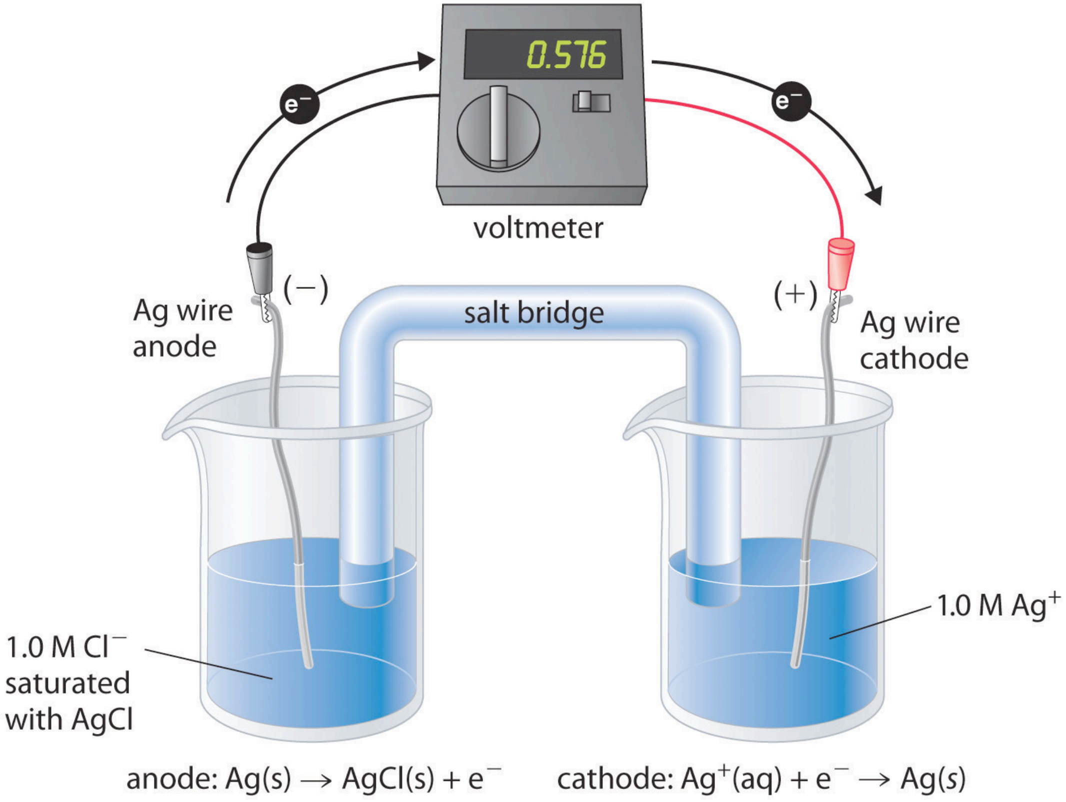
Quantification of Oxidizing and Reducing Strengths

We know that MnO_4^- is a powerful oxidant and $[Cr(OH_2)_6]^{2+}$ is a powerful reductant.

But how do we quantify oxidising and reducing strength?

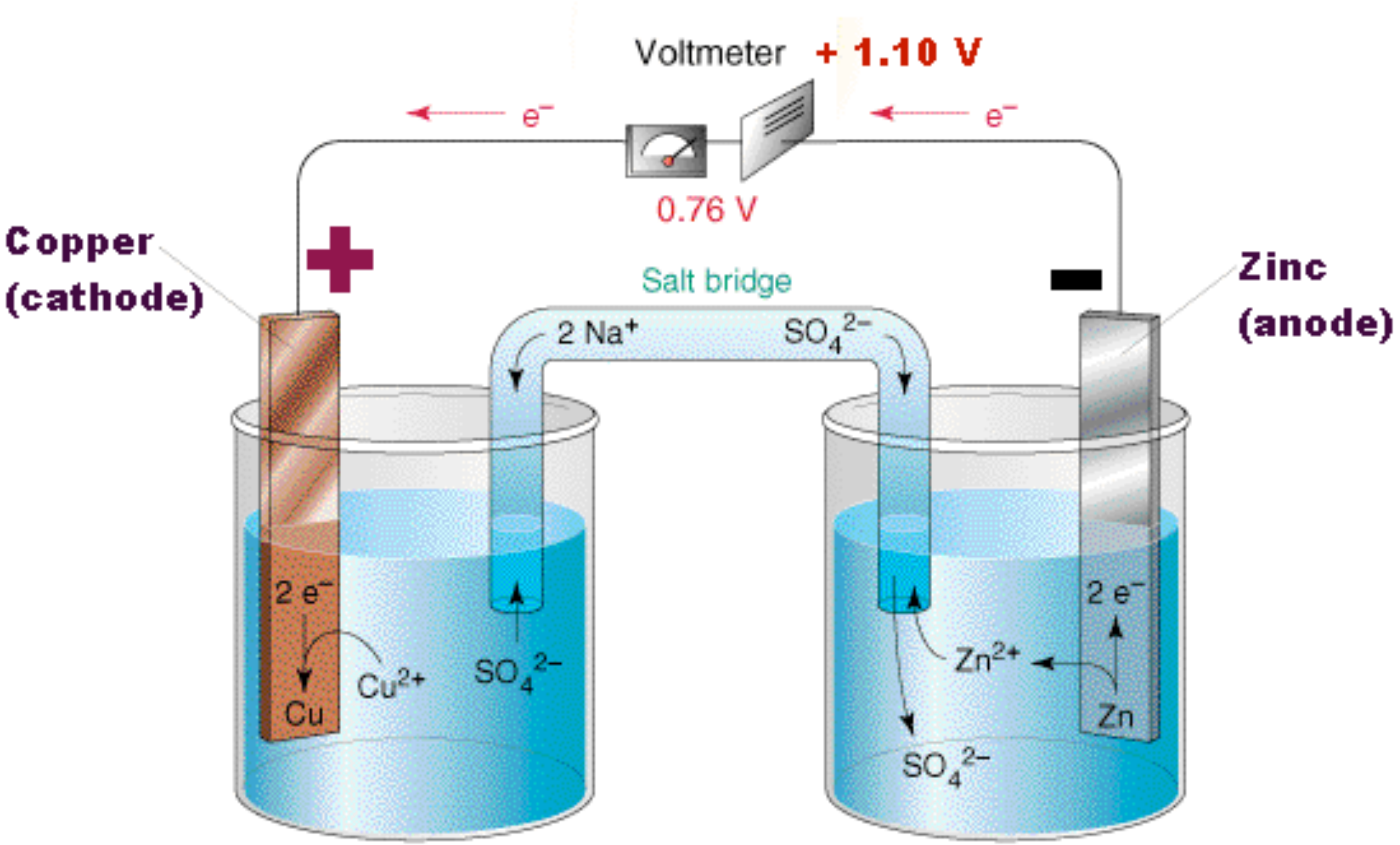
The answer: Using a scale of standard redox potentials, E_o

These are best envisaged as part of an electrochemical cell – the driving force in a battery



Quantification of Oxidizing and Reducing Strengths

Consider the interaction of Cu^{2+}/Cu and Zn^{2+}/Zn in the **Daniell Cell**



$Cu^{2+} + 2\,e^- \longrightarrow Cu(s)$ **+0.34 V**

$Zn(s) \longrightarrow Zn^{2+} + 2\,e^-$ **+ 0.76 V**

$Cu^{2+} + Zn(s) \longrightarrow Zn^{2+} + Cu(s)$

Reaction is spontaneous as ΔG^o is negative

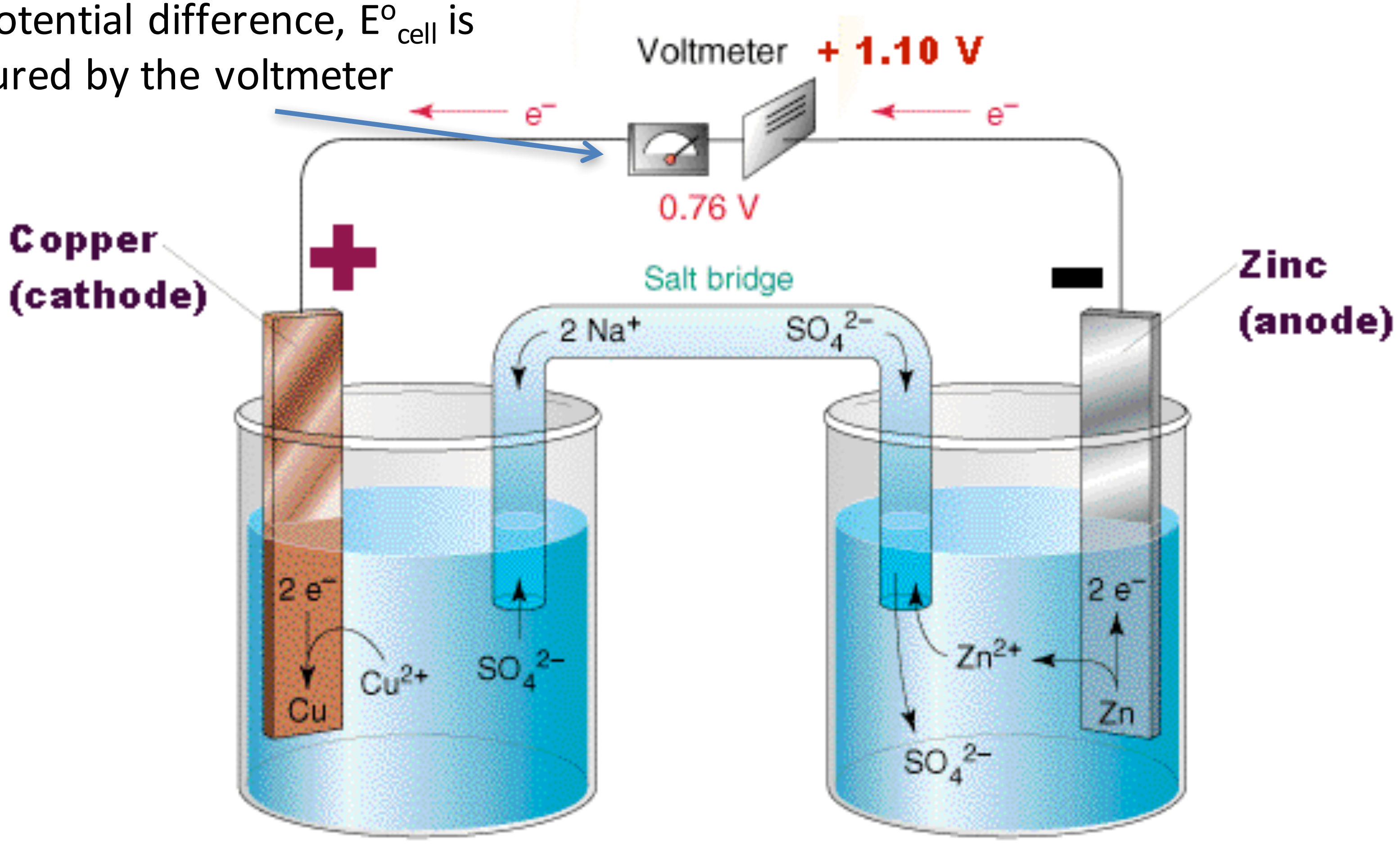
Quantification of Oxidizing and Reducing Strengths

This is made up of two half reactions:

$$Cu^{2+}_{aq} + 2e^- \rightleftharpoons Cu(s) \qquad E^o_{Cu(II)/Cu}$$

$$Zn^{2+}_{aq} + 2e^- \rightleftharpoons Zn(s) \qquad E^o_{Zn(II)/Zn}$$

The potential difference, E^o_{cell} is measured by the voltmeter



$Cu^{2+} + 2e^- \rightarrow Cu(s)$ **+0.34 V**

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ **+ 0.76 V**

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

Reaction is spontaneous as ΔG^o is negative

Quantification of Oxidizing and Reducing Strengths

This is made up of two half reactions:

$$Cu^{2+}_{aq} + 2\,e^- \rightleftharpoons Cu(s) \qquad E^o_{Cu(II)/Cu}$$

$$Zn^{2+}_{aq} + 2\,e^- \rightleftharpoons Zn(s) \qquad E^o_{Zn(II)/Zn}$$

The potential difference, E^o_{cell} is measured by the voltmeter

$$\mathbf{E^o_{cell} = E^o_{reduction} - E^o_{oxidation} = E^o_{cathode} - E^o_{anode}}$$

The potential difference, E^o_{cell} is defined as the standard cell potential under standard conditions:

- Unit activity (which means dilution solutions so activities approximate concentrations)
- 1 bar pressure of any gaseous component
- All solid components are in their standard states
- T = 298 K

$\Delta G^o_{cell} = -nFE^o_{cell}$

where F is the Faraday constant = 96487 C mol^{-1}

n is the number of electrons transferred in the reaction

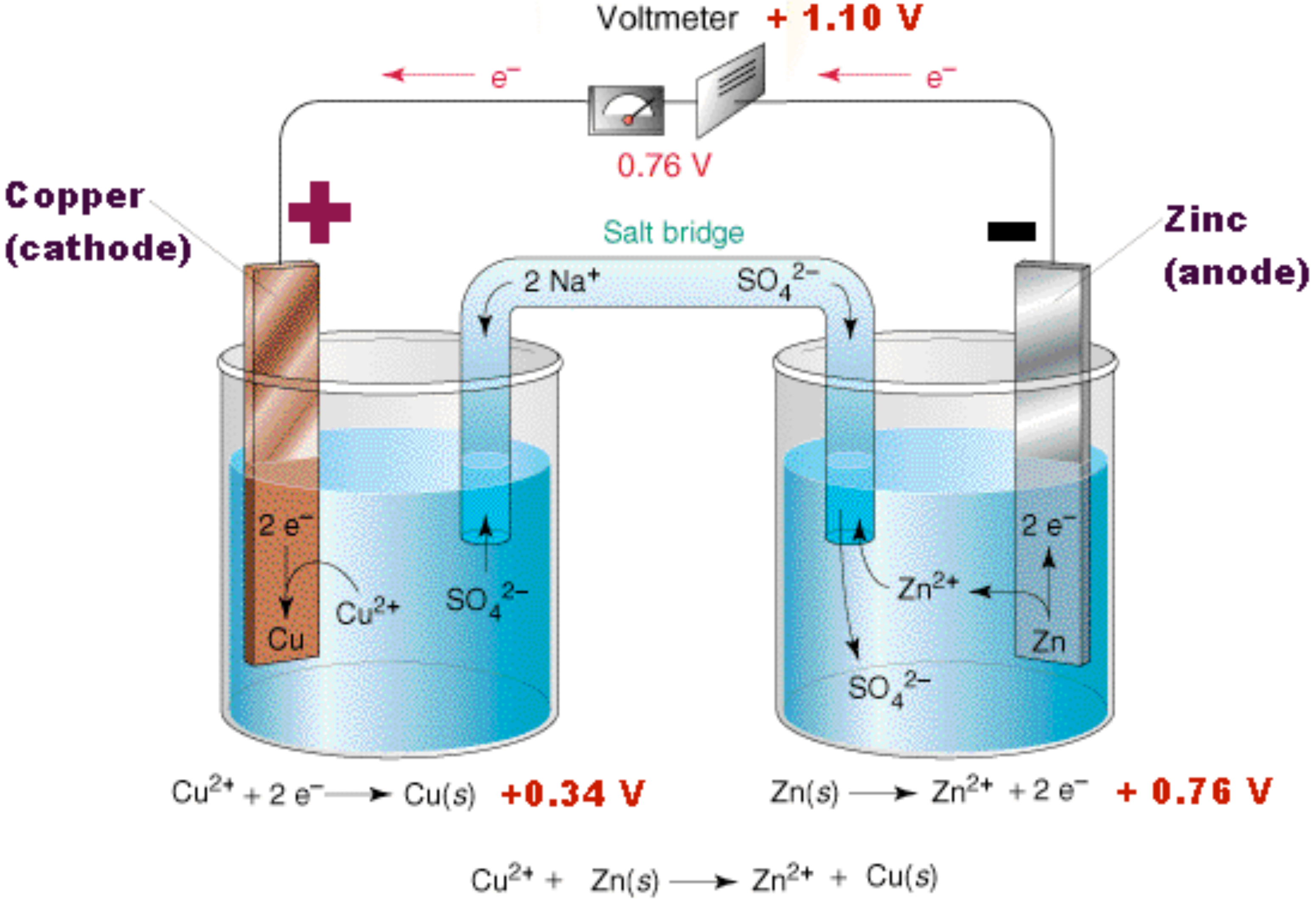
For a cell reaction to be thermodynamically favourable E^o_{cell} must be positive so that ΔG^o_{cell} is negative

Quantification of Oxidizing and Reducing Strengths

E^o_{cell} at 298 K = 1.10 V

So $\Delta G^o_{cell} = -nFE^o_{cell} = -2*96487*1.10 = -212\ 267$ J per mol reaction = -212 KJ mol^{-1}

$\Delta G^o_{cell} = -RT\ \ln(K_{cell})$ and so $K_{cell} = 1.50 \times 10^{37}$ - so reaction is highly favoured!



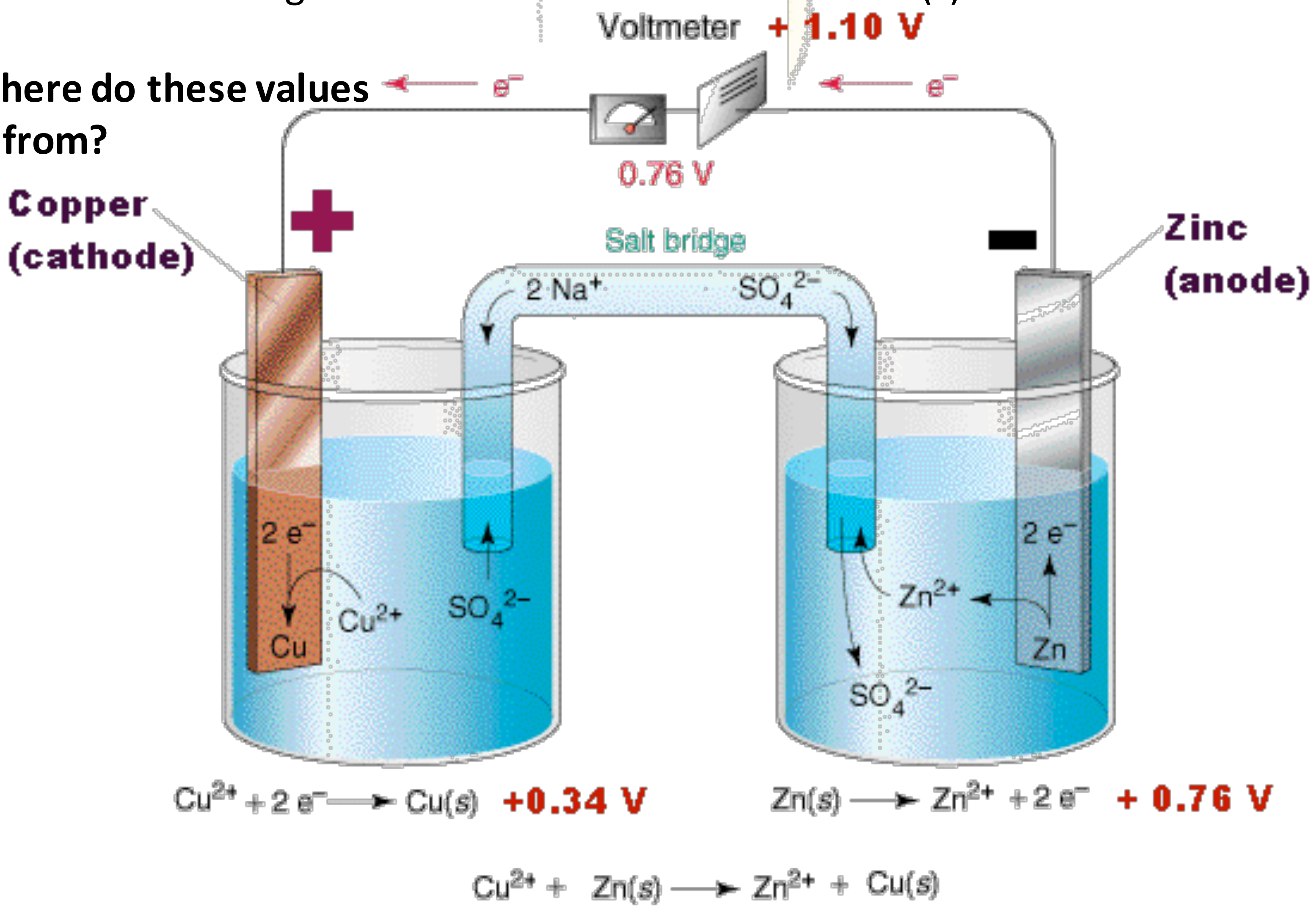
Quantification of Oxidizing and Reducing Strengths

E^o_{cell} at 298 K = 1.10 V

There is +0.34 V driving the reaction due to reduction of Cu^{2+}

There is +0.76 V driving the reaction due to oxidation of Zn(s)

But where do these values come from?

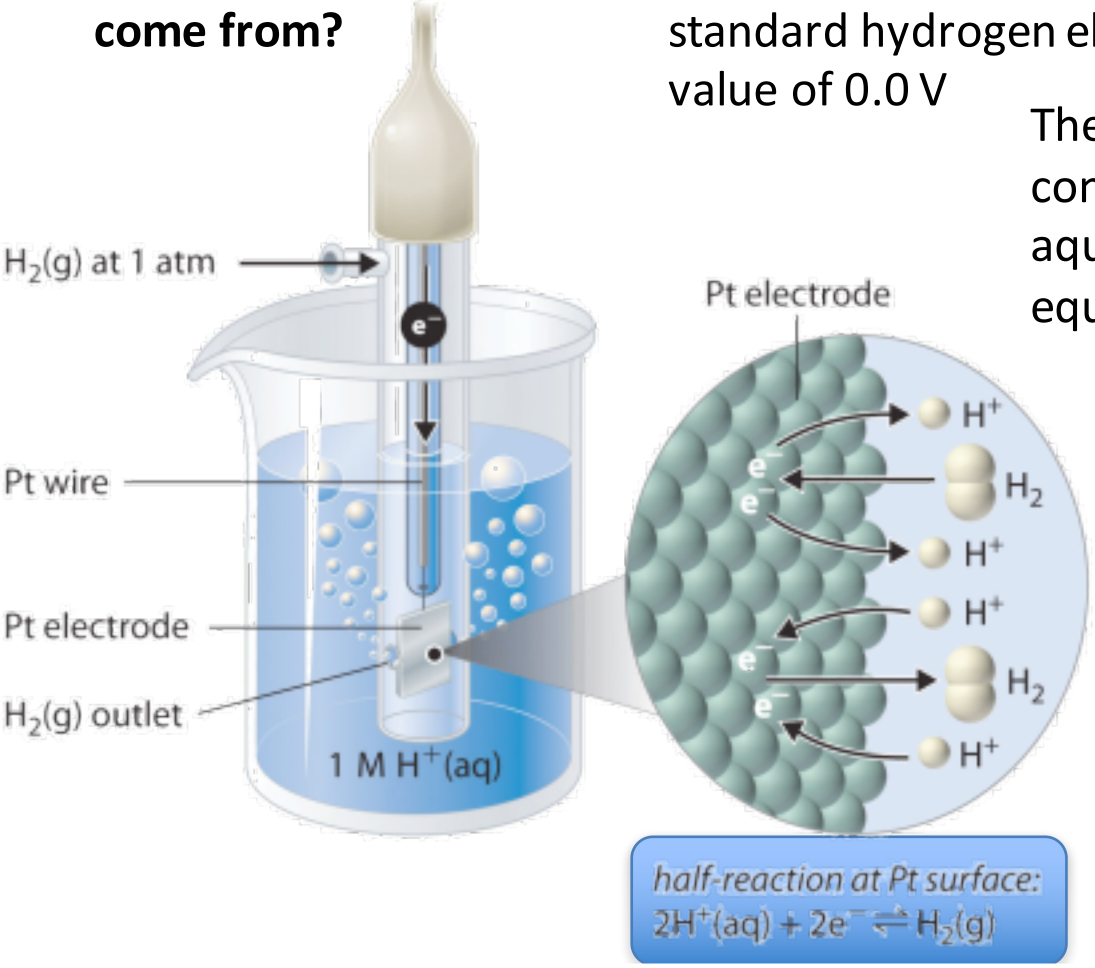


Quantification of Oxidizing and Reducing Strengths

E^o_{cell} at 298 K = 1.10 V
There is +0.34 V driving the reaction due to reduction of Cu^{2+}
There is +0.76 V driving the reaction due to oxidation of Zn(s)

But where do these values come from?

All E° values are related on a scale to the cell potential of the standard hydrogen electrode (SHE), which is arbitrarily set at a value of 0.0 V



The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm.

Half-cell potentials are **intensive properties**, namely independent of the amount of the reacting species.

Quantification of Oxidizing and Reducing Strengths

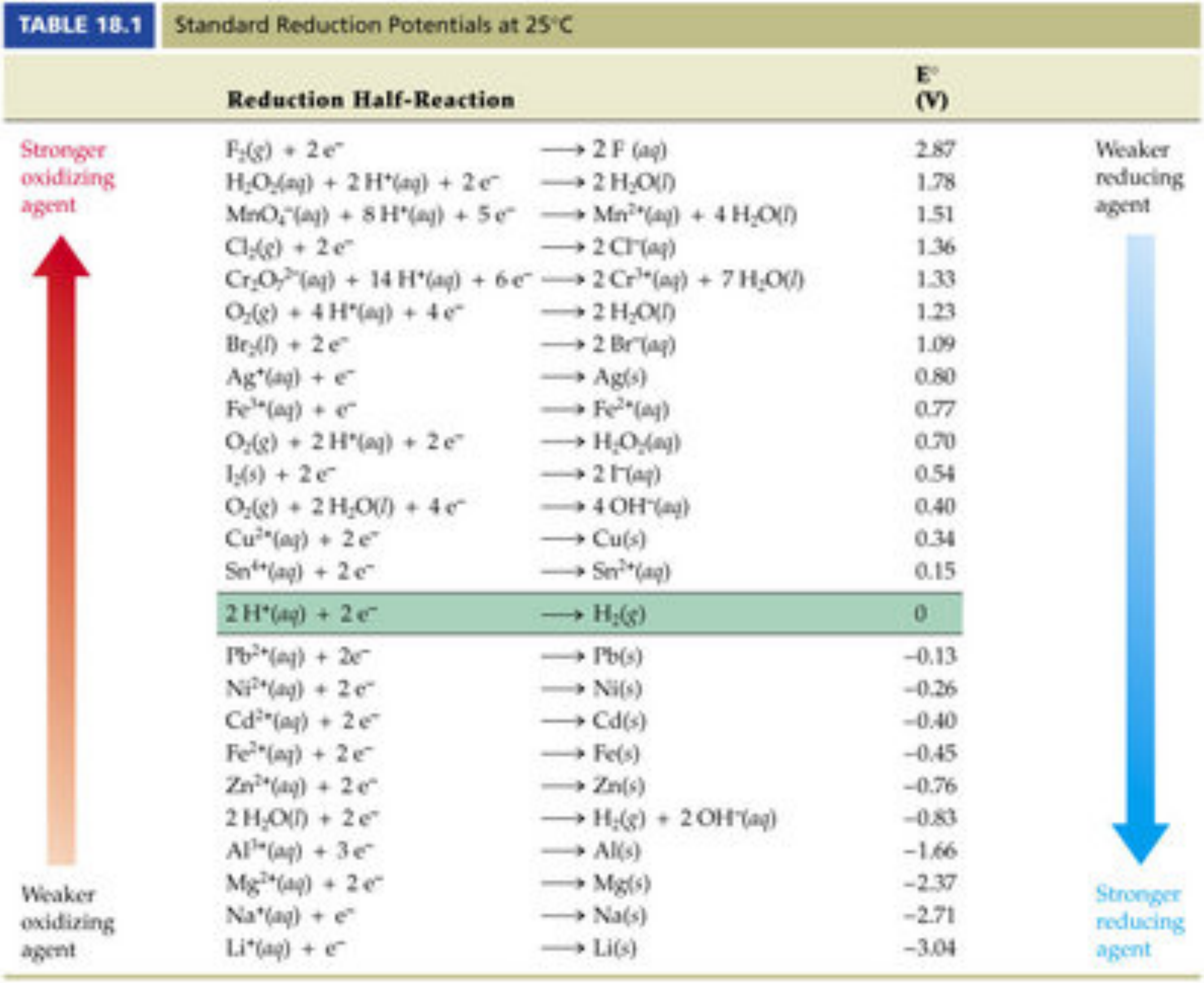


TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51	
	$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33	
	$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23	
	$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54	
	$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Quantification of Oxidizing and Reducing Strengths

CH3514

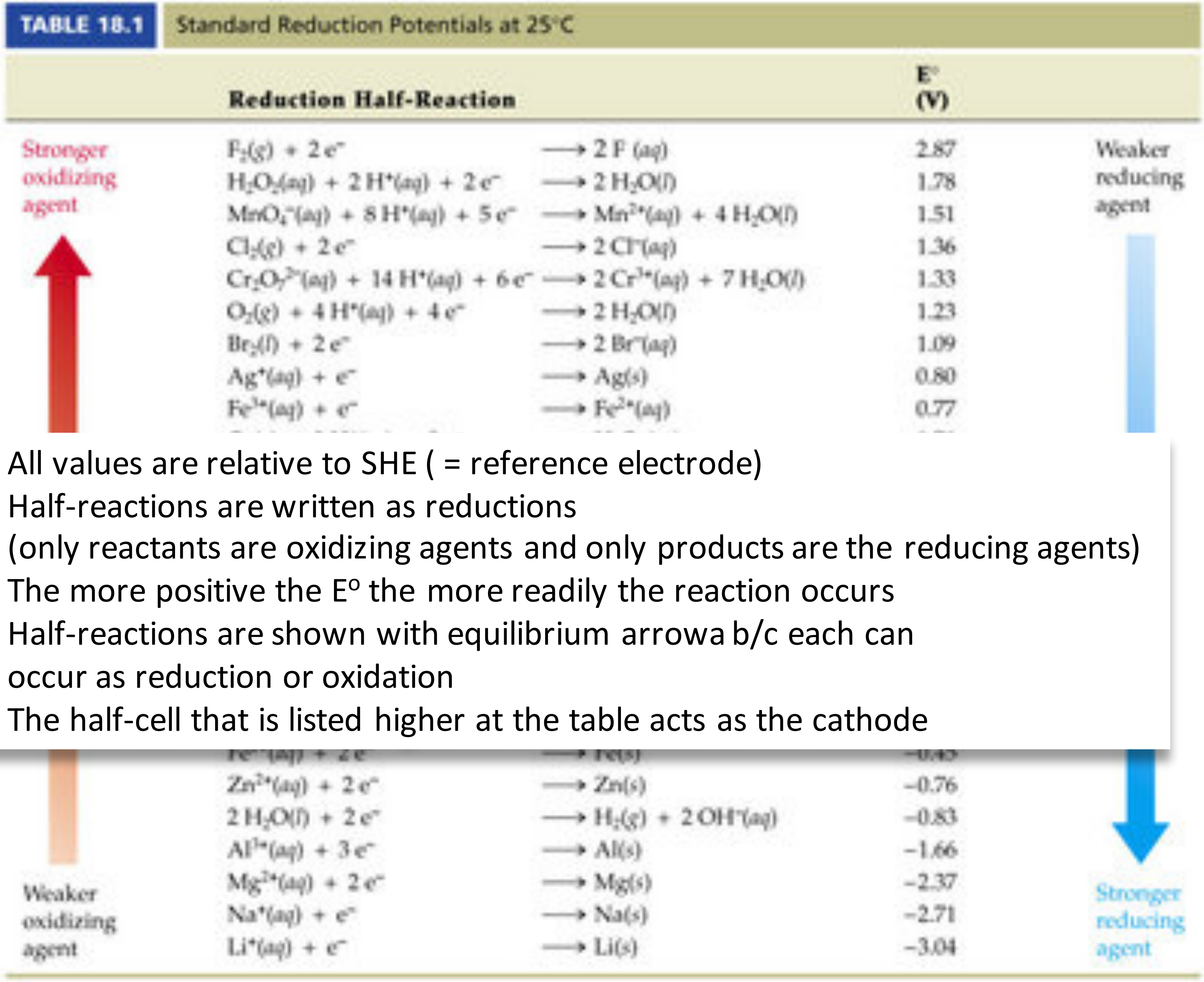


TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
Weaker oxidizing agent	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	Stronger reducing agent
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

1. All values are relative to SHE (= reference electrode)
2. Half-reactions are written as reductions
   (only reactants are oxidizing agents and only products are the reducing agents)
3. The more positive the E° the more readily the reaction occurs
4. Half-reactions are shown with equilibrium arrowa b/c each can
   occur as reduction or oxidation
5. The half-cell that is listed higher at the table acts as the cathode

Quantification of Oxidizing and Reducing Strengths

E^o_{cell} at 298 K = 1.10 V
There is +0.34 V driving the reaction due to reduction of Cu^{2+}
There is +0.76 V driving the reaction due to oxidation of Zn(s)

By combining the SHE with another half cell, e.g., $Cu^{2+}_{aq}/Cu(s)$, the E° can be determined from the measured cell potential E^o_{cell}

We can then show:

$$Cu^{2+}_{aq} + 2\,e^- \rightleftharpoons Cu(s) \qquad E^o_{Cu(II)/Cu} = +\,0.34\ V$$

$$Zn^{2+}_{aq} + 2\,e^- \rightleftharpoons Zn(s) \qquad E^o_{Zn(II)/Zn} = -\,0.76\ V$$

We can now see why Zn(s) readily reduces Cu^{2+}_{aq} and provides the huge driving force for the **Daniell cell**

$$\underset{\substack{\text{stronger}\\\text{reducing}\\\text{agent}}}{Zn\,(s)} + \underset{\substack{\text{stronger}\\\text{oxidizing}\\\text{agent}}}{Cu^{2+}(aq)} \rightarrow \underset{\substack{\text{weaker}\\\text{oxidizing}\\\text{agent}}}{Zn^{2+}(aq)} + \underset{\substack{\text{weaker}\\\text{reducing}\\\text{agent}}}{Cu\,(s)}$$

Quantification of Oxidizing and Reducing Strengths

Let’s look at a different reaction. Let’s consider the well known titration reaction of the reduction MnO_4^- with Fe^{2+}_{aq} under standard conditions (1 M H^+, 298 K)

The half reactions are:

$$Fe^{3+}_{aq} + e^- \rightleftharpoons Fe^{2+}_{aq} \qquad E^o = +0.77\ V$$

$$MnO_4^-{}_{aq} + 8\,H^+_{aq} + 5\,e^- \rightleftharpoons Mn^{2+}{}_{aq} + 4\,H_2O\,(l) \qquad E^o = +1.51\ V$$

We can now see that from the relative E^0 values that the spontaneous reaction is:

$$MnO_4^-{}_{aq} + 8\,H^+_{aq} + 5\,Fe^{2+}_{aq} \overset{E^o_{cell}}{\rightleftharpoons} Mn^{2+}_{aq} + 5\,Fe^{3+}_{aq} + 4\,H_2O\,(l)$$

$E^o_{cell} = E^o_{red} – E^o_{ox} = 1.51 – (+0.77) = 0.74$ V
$\Delta G^o_{cell} = -357.03$ KJ mol^{-1} (very favourable)

Quantification of Oxidizing and Reducing Strengths

Let’s now look at a different process, which is the oxidation of Fe(s) by $Cl_{2\,aq}$.

The half reactions are:

$$Fe^{2+}_{aq} + 2\,e^- \rightleftharpoons Fe(s) \qquad E^o = -0.44\ V$$

$$Fe^{3+}_{aq} + 3\,e^- \rightleftharpoons Fe(s) \qquad E^o = -0.04\ V$$

$$Cl_{2\,aq} + 2\,e^- \rightleftharpoons 2\,Cl^-_{aq} \qquad E^o = +1.36\ V$$

These data indicate that two reactions are possible:

$$Cl_{2\,aq} + Fe(s) \rightleftharpoons 2\,Cl^-_{aq} + Fe^{2+}_{aq} \qquad E^o_{cell} = +1.80\ V$$

$$3Cl_{2\,aq} + 2\,Fe(s) \rightleftharpoons 6\,Cl^-_{aq} + 2\,Fe^{3+}_{aq} \qquad E^o_{cell} = +1.40\ V$$

Both E^o_{cell} values are positive and from their magnitude one might suppose the first reaction is favoured over the second…

Quantification of Oxidizing and Reducing Strengths

But what really counts is ΔG^o_{cell}

Can show that the second reaction is favoured by consider the ΔG^o_{cell} values for the two processes, which take into account the number of electrons involved

$$Cl_{2\,aq} + Fe(s) \rightleftharpoons 2\,Cl^-_{aq} + Fe^{2+}_{aq} \qquad E^o_{cell} = +1.80\text{ V}$$

$$\Delta G^o_{cell} = -\,n\,F\,E^o_{cell} = -\,2 \times 96487 \times 1.80 = -\,347\text{ kJ mol}^{-1}$$

$$3Cl_{2\,aq} + 2\,Fe(s) \rightleftharpoons 6\,Cl^-_{aq} + 2\,Fe^{3+}_{aq} \qquad E^o_{cell} = +1.40\text{ V}$$

$$\Delta G^o_{cell} = -\,n\,F\,E^o_{cell} = -\,6 \times 96487 \times 1.40 = -\,810\text{ kJ mol}^{-1}$$

Therefore second reaction favoured by **~ 500 kJ mol^{-1} !**

Quantification of Oxidizing and Reducing Strengths

So far we have been looking at systems under standard conditions.
What happens if we change the pH?

1st example: Reduction of MnO_4^-

$$MnO_4^-{}_{aq} + 8\,H^+_{aq} + 5\,e^- \rightleftharpoons Mn^{2+}_{aq} + 4\,H_2O\,(l) \quad E^o = +1.51\ V$$

Here E^o refers to the condition $[H^+] = 1\ mol\ dm^{-3}$, pH = 0
Because of the consumption of H^+ ions, the above E^o will vary with pH.

What would be the measured E value for the above at pH 2.5 at 298K ?

Quantification of Oxidizing and Reducing Strengths
The Nernst Equation

So E drops as pH increases!

We can calculate E under any conditions using the Nernst Equation

$$\text{oxidant} + n\,e^- + y\,H^+ \rightleftharpoons \text{reductant}$$

$$\underset{\text{measured}}{E} = \underset{\text{standard}}{E^o} - \frac{R\,T}{n\,F}\ln\left(\frac{[\text{reductant}]}{[\text{oxidant}]\,[H^+]^y}\right)$$

For the reduction of MnO_4^-:

$$\underset{\text{measured}}{E} = 1.51 - \frac{R\,T}{n\,F}\ln\left(\frac{[Mn^{2+}{}_{aq}]}{[MnO_4^-]\,[H^+]^8}\right)$$

At pH = 2.5 = $-\log_{10}([H^+])$; $[H^+] = 3.2 \times 10^{-3}$ M:

$$\underset{\text{measured}}{E} = 1.51 - \frac{8.314 \times 298}{5 \times 96487}\ln\left(\frac{[Mn^{2+}{}_{aq}]}{[MnO_4^-]\,[3.2 \times 10^{-3}]^8}\right)$$

At equilibrium $[Mn^{2+}{}_{aq}] = [MnO_4^-]$ and $E = E_{eq}$

$$E_{eq} = 1.51 - 5.13 \times 10^{-3}\ \ln\ (9.09 \text{ X } 10^{19}) = \mathbf{1.27}$$

Quantification of Oxidizing and Reducing Strengths

So far we have been looking at systems under standard conditions.
What happens if we change the pH?

2nd example: Reduction of $Zn^{2+}{}_{aq}$

$$Zn^{2+}_{aq} + 2\ e^{-} \rightleftharpoons Zn(s)$$

$E^{o}_{Zn(II)/Zn}$

pH 0	pH 14
-0.76 V	-1.20 V

No $[H^{+}]$ consumption here – so why the change?

The reason is that at pH 0 the Zn^{2+} species is $[Zn(OH_2)_6]^{2+}$

but at pH 14 the species is $[Zn(OH)_4]^{2-}$

So the Zn^{2+} species being reduced is different!

Quantification of Oxidizing and Reducing Strengths

So far we have been looking at systems under standard conditions.
What happens if we change the pH?

3rd example: $Mn^{3+}/Mn^{2+}{}_{aq}$ – an example where pH affects redox behaviour

At **pH 0**: Mn^{3+} exists as $[Mn(OH_2)_6]^{3+}$ and can oxidise $H_2O \rightarrow O_2$

$$[Mn(OH_2)_6]^{3+} + e^- \rightleftharpoons [Mn(OH_2)_6]^{2+} \qquad E^o = +1.54\ V$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^o = +1.23\ V$$

$E^o_{cell} = 1.54 - 1.23 = 0.31\ V$ (favourable)

$\Delta G^o_{cell} = -nFE^o_{cell} = -4 * 96487 * 0.31\ J\ mol^{-1} = -120\ KJ\ mol^{-1}$

Quantification of Oxidizing and Reducing Strengths

So far we have been looking at systems under standard conditions.
What happens if we change the pH?

3rd example: $Mn^{3+}/Mn^{2+}{}_{aq}$ – an example where pH affects redox behaviour

At **pH 14**: Mn^{III} and Mn^{II} are now present as the hydroxo complexes; $Mn(OH)_{2/3}(s)$

$$Mn(OH)_3(s) + e^- \rightleftharpoons Mn(OH)_2(s) + OH^-_{aq} \qquad E^o = -0.27\ V$$

$$O_2 + 2H_20 + 4e^- \rightleftharpoons 4OH^-_{aq} \qquad E^o = +0.40\ V$$

$[OH^-] = 1$ mol dm^{-3}, pH = 14

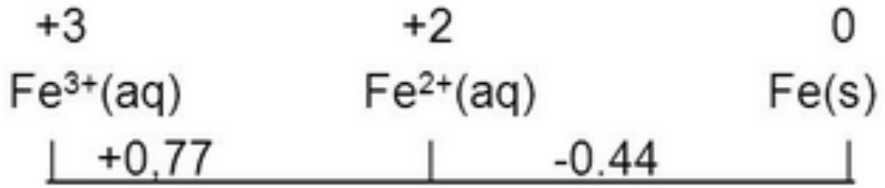
Now O_2 is the oxidant and $E^o_{cell} = 0.4 - (-0.27) = 0.67$ V (favourable)

$\Delta G^o_{cell} = -nFE^o_{cell} = -4*96487*0.67\ J\ mol^{-1} = -259\ KJ\ mol^{-1}$

Quantification of Oxidizing and Reducing Strengths
Latimer Diagrams

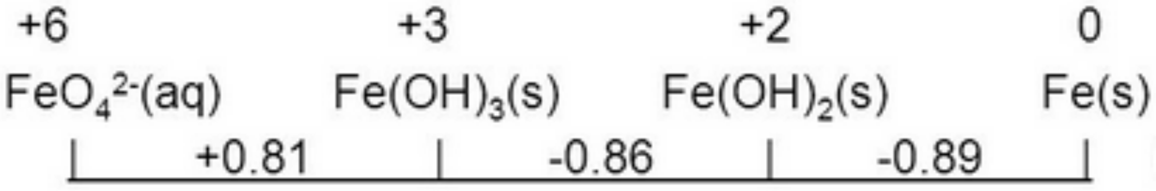
When several oxidation states exist for a particular metal a convenient method of representing the respective E° values is in the form of a Latimer diagram

1^{st} example: Iron



pH = 0

Using ΔG° values can show using the above that $E^o(Fe^{3+}_{aq}/Fe(s)) = -0.04$ V



pH = 14

Recall Hess's Law: $\Delta G_{overall} = \Sigma\ \Delta G_{individual\ steps}$

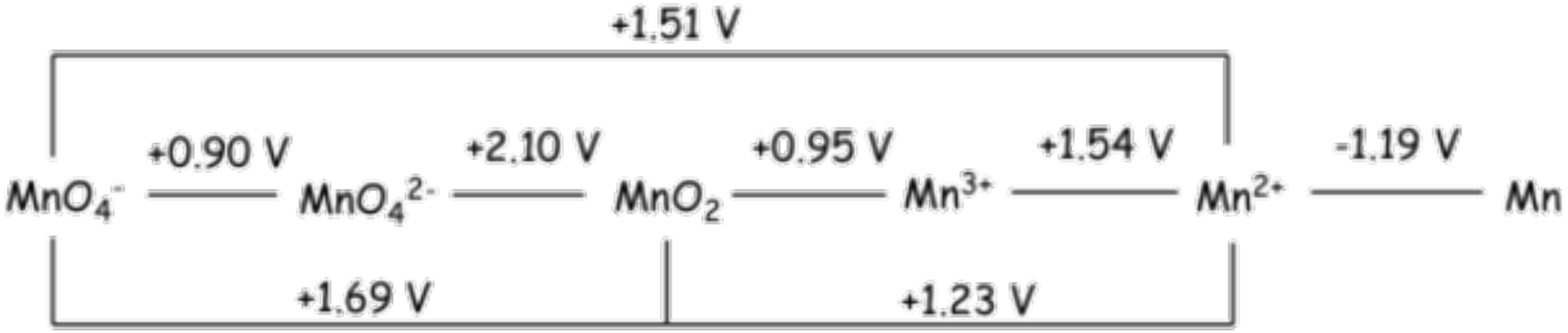
Housecroft and Sharpe, page 227

Quantification of Oxidizing and Reducing Strengths
Latimer Diagrams

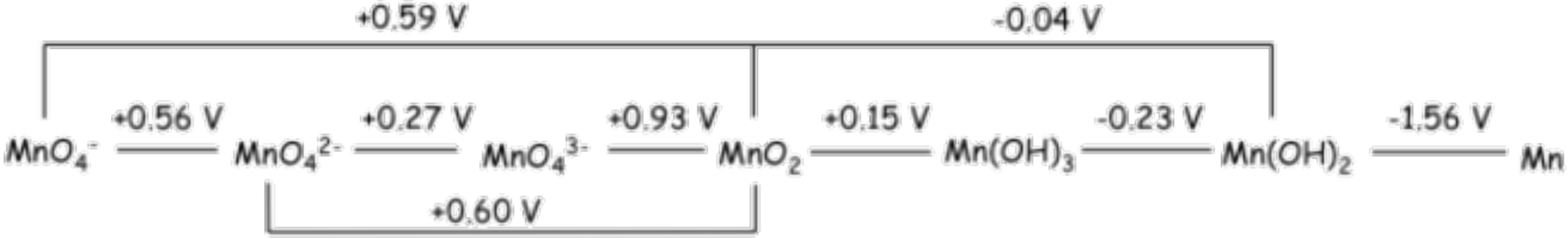
When several oxidation states exist for a particular metal a convenient method of representing the respective E° values is in the form of a Latimer diagram

With multiple Latimer diagrams, one can illustrate the change in E° with pH

2nd example: Manganese



pH = 0



pH = 14

Housecroft and Sharpe, page 226

University of St Andrews

CH3514

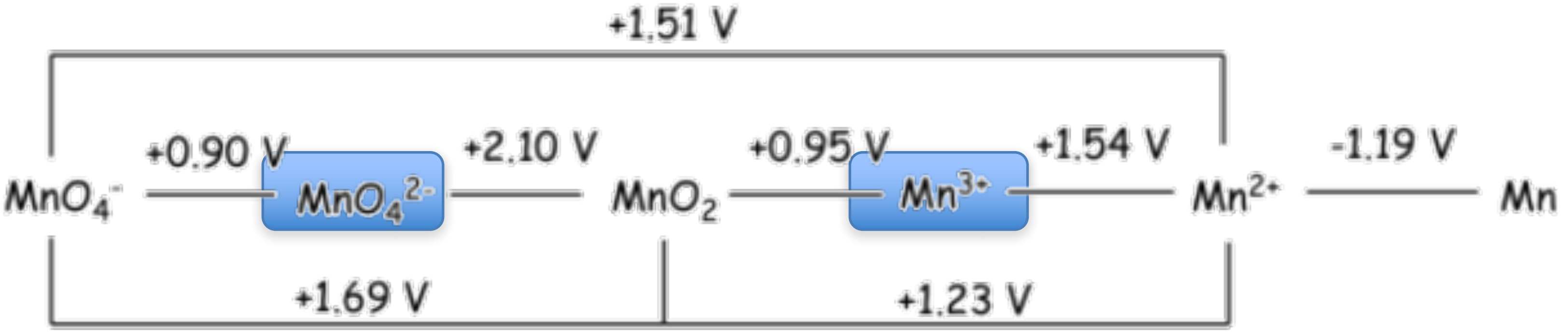
Quantification of Oxidizing and Reducing Strengths
Latimer Diagrams

When several oxidation states exist for a particular metal a convenient method of representing the respective Eº values is in the form of a Latimer diagram

With multiple Latimer diagrams, one can illustrate the change in Eº with pH

2nd example: Manganese

Let's have a closer look:



pH = 0

When a given oxidation state has a higher (more positive) Eº for its **reduction** than for its oxidation it is thermodynamically unstable to disproportionation to give the two oxidation states either side.

One can show ΔGº for this process is negative

Do any of the species above satisfy this criterion? **YES**

Housecroft and Sharpe, page 226

CH3514

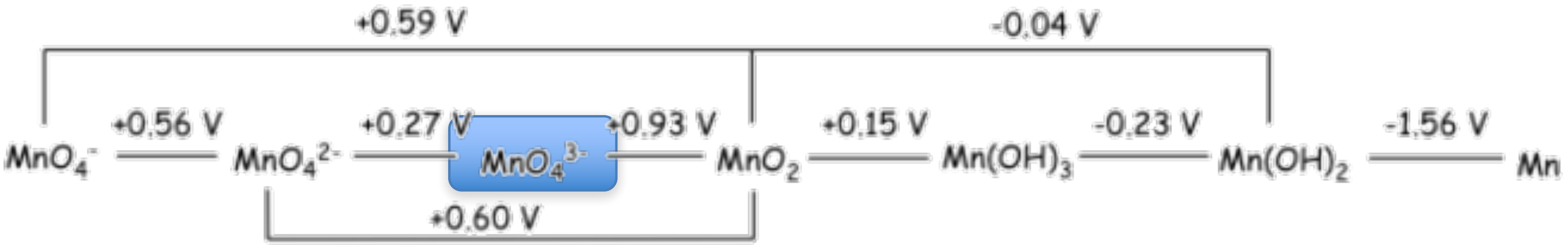
Quantification of Oxidizing and Reducing Strengths
Latimer Diagrams

When several oxidation states exist for a particular metal a convenient method of representing the respective E° values is in the form of a Latimer diagram

With multiple Latimer diagrams, one can illustrate the change in E° with pH

2nd example: Manganese

Let's have a closer look:



pH = 14

When a given oxidation state has a higher (more positive) E° for its **reduction** than for its oxidation it is thermodynamically unstable to disproportionation to give the two oxidation states either side.

One can show ΔG^o for this process is negative

Do any of the species above satisfy this criterion? **YES**

In this case: MnO_4^{2-} and Mn^{3+} in the form of $Mn(OH)_3$(s), are now stable towards disproportionation

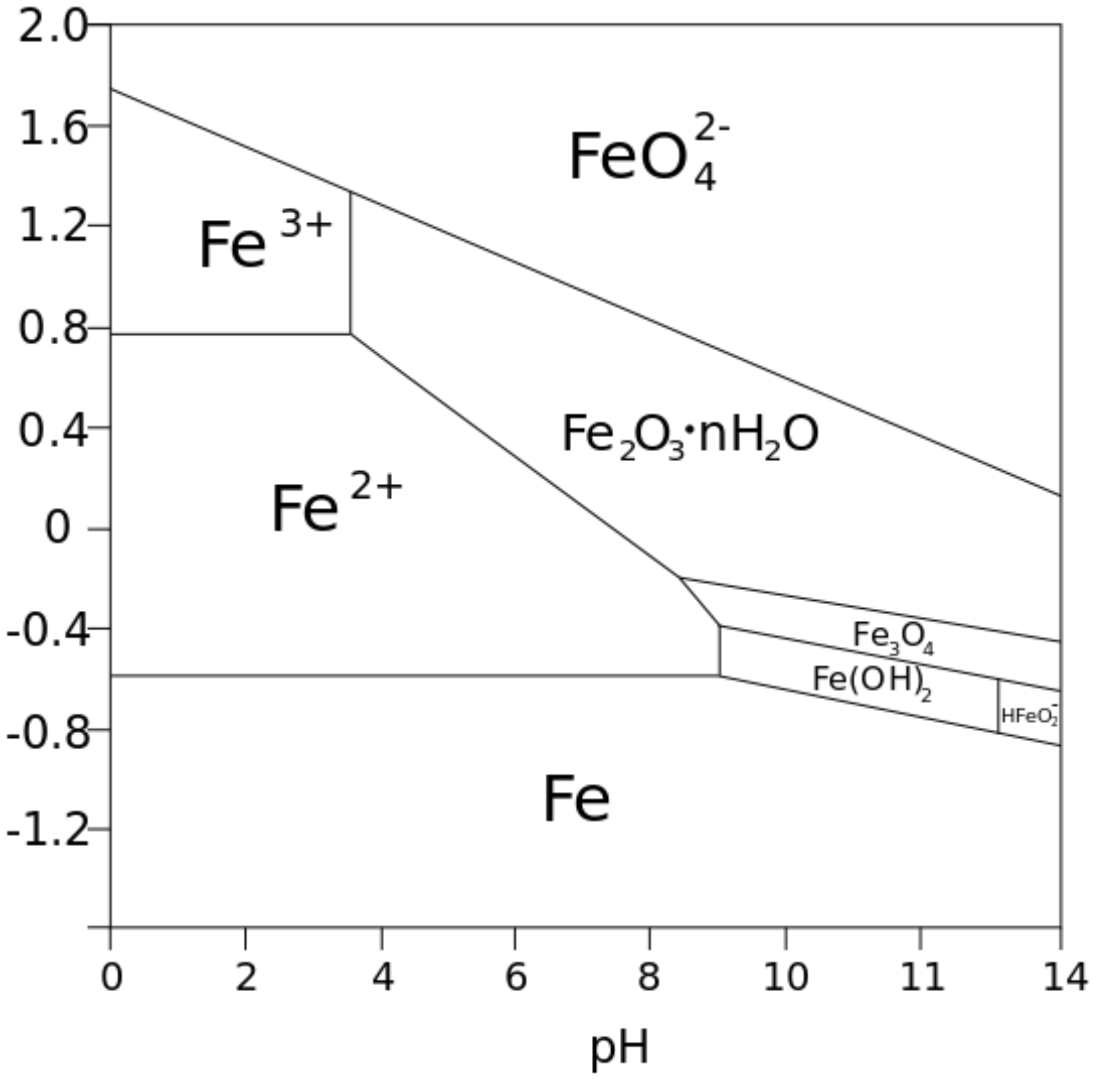
Housecroft and Sharpe, page 226

Quantification of Oxidizing and Reducing Strengths
Pourbaix Diagrams

A Pourbaix Diagram condenses the information available in Latimer Diagrams across all pH ranges.

Nernst Equation

$$E_H = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$



Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams

A convenient way of representing redox behaviour is to graphically plot ΔG^o versus the oxidation number

Recall that $\Delta G^o = - n\ F\ E^o$
So $\Delta G^o/F = -nE^o$

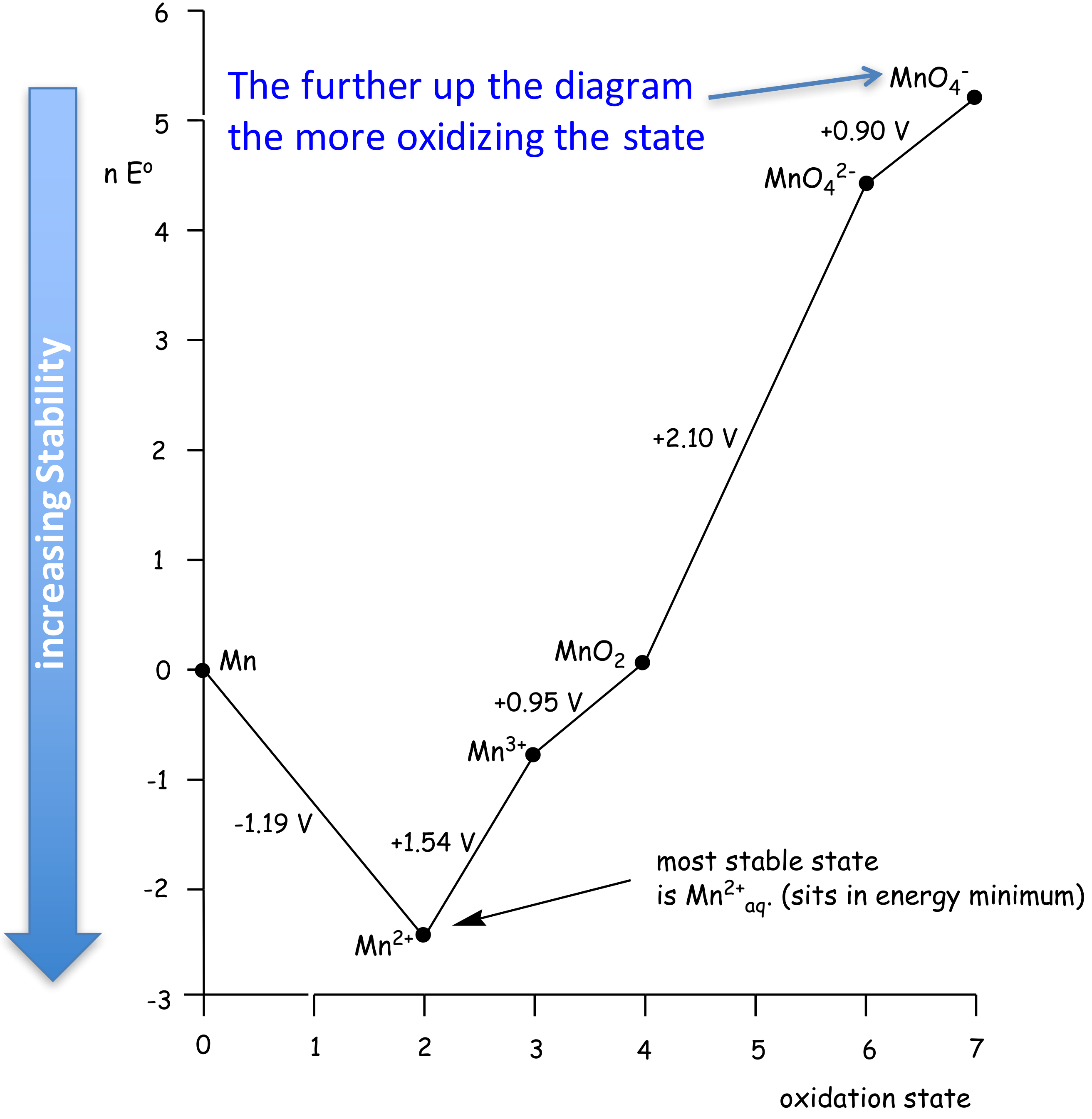
The FE diagrams can be used to predict redox behaviour

So if we plot nE^o vs oxidation number then the slope of the line drawn between two oxidation states, separation n, will give E^o for that process.

Housecroft and Sharpe, page 227-230

Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams

Example 1: Mn at pH 0



The further up the diagram the more oxidizing the state

most stable state is Mn$^{2+}_{aq.}$ (sits in energy minimum)

Housecroft and Sharpe, page 227-230

University of St Andrews

Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams

Example 1: Mn at pH 0

$MnO_4^{2-} + 4\,H^+ + 2\,e^- \rightleftharpoons MnO_2 + 2H_2O \quad E^o = +2.10V$

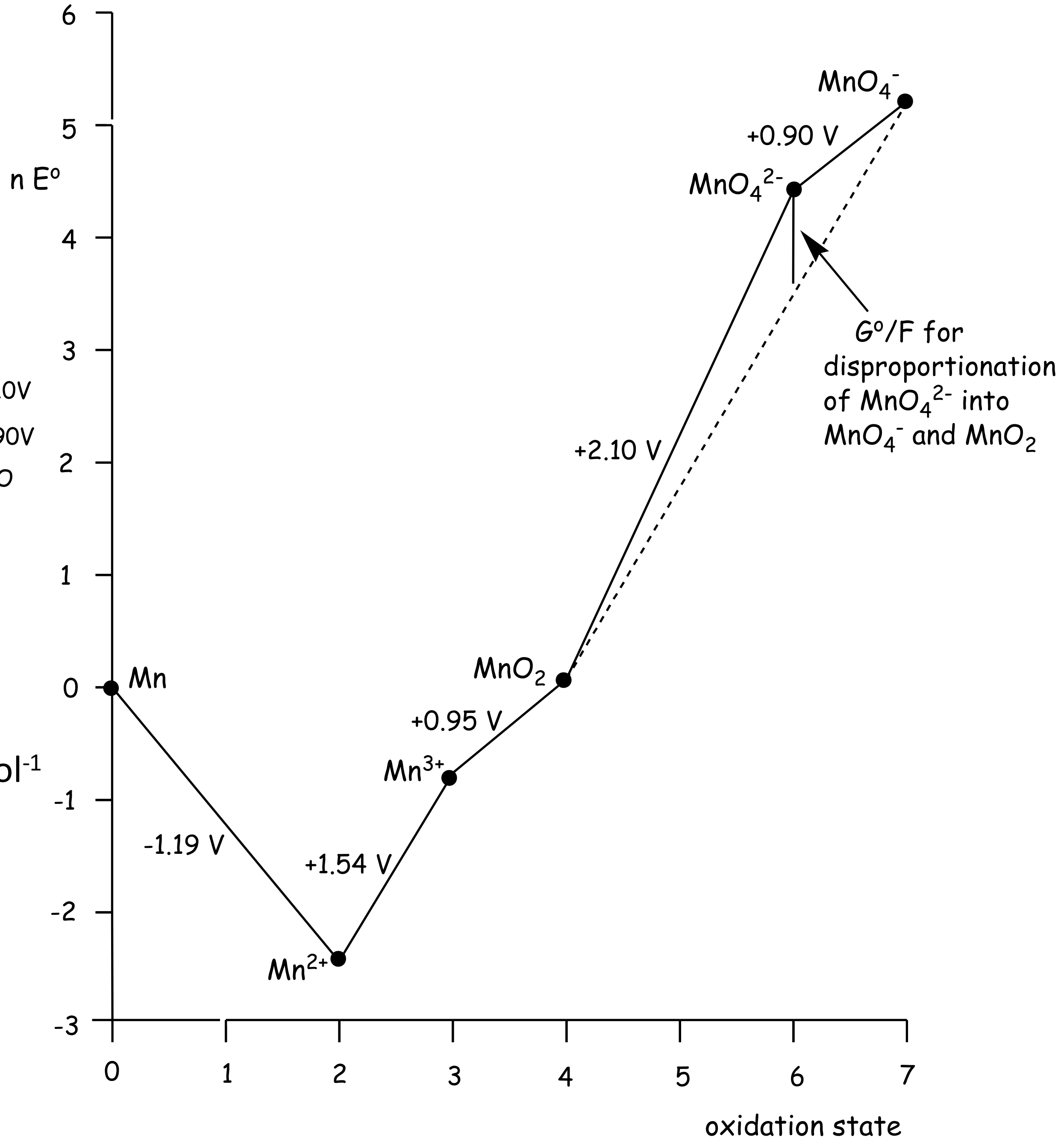
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-} \quad E^o = +0.90V$

$3\,MnO_4^{2-} + 4\,H^+ \rightleftharpoons MnO_2 + 2\,MnO_4^- + 2H_2O$

$E^o_{disp} = 2.10 - 0.90 = +1.20\ V$

$G^o_{disp} = -231.5\ kJ\ mol^{-1}$

$\Delta G^o = -nFE^o = -2*96487*1.2 = -231.5\ KJ\ mol^{-1}$

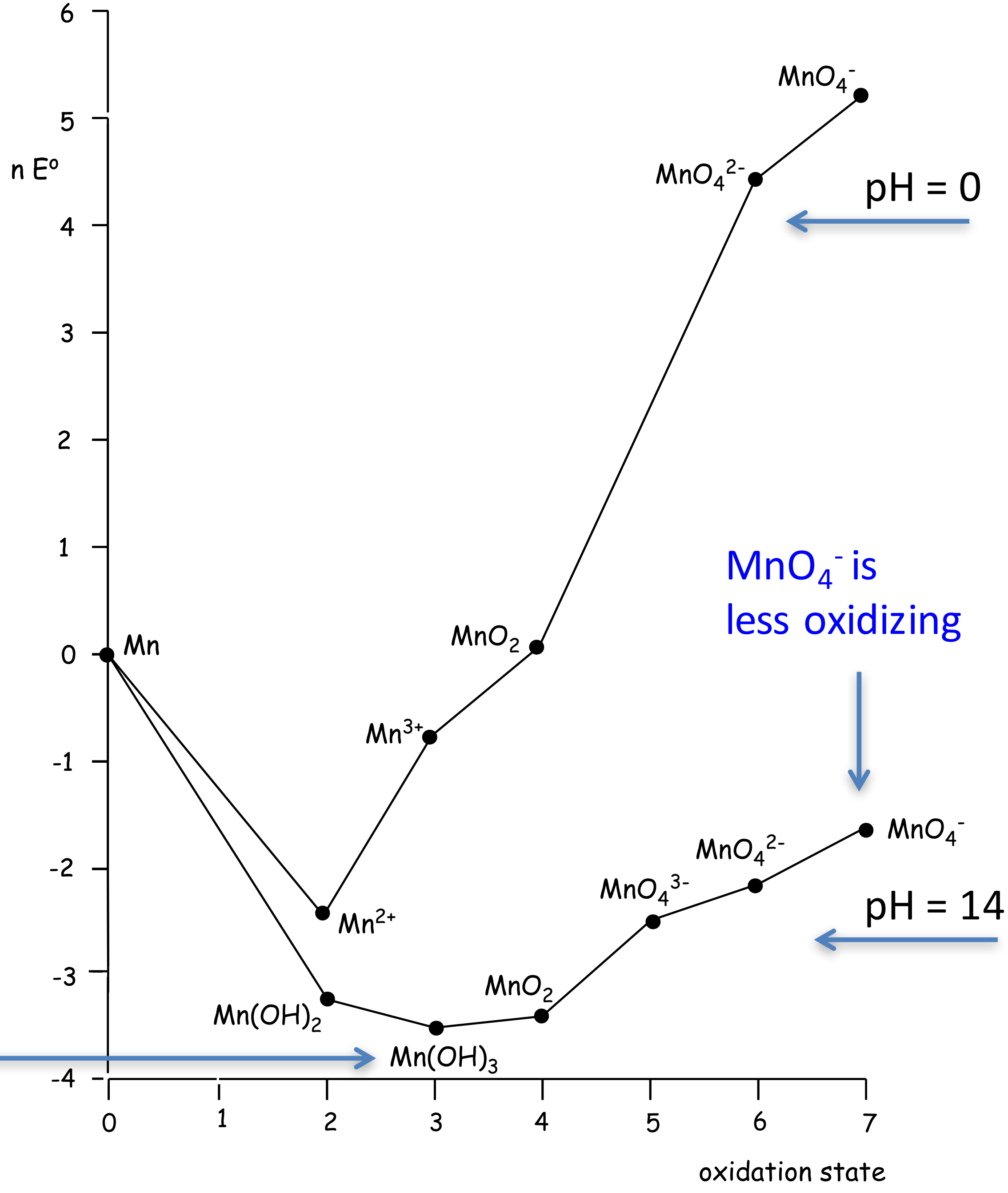


Housecroft and Sharpe, page 227-230

Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams

Example 1: Mn at pH 0 and pH 14

We can also illustrate the effects of pH on the redox behaviour



pH = 0

MnO_4^- is less oxidizing

pH = 14

$Mn(OH)_3$ is now the most stable state

Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams

Which pH condition is best for MnO_4^- titrations?

pH = 0 Use of acid solution avoids MnO_2(s) production

	E^o / V	G^o / kJ mol^{-1}
$MnO_4^-{}_{aq} + 8\,H^+{}_{aq} + 5\,e^- \rightleftharpoons Mn^{2+}{}_{aq} + 4\,H_2O\,(l)$	+ 1.51	-728.5
$MnO_4^-{}_{aq} + 4\,H^+{}_{aq} + 3\,e^- \rightleftharpoons MnO_2(s) + 2\,H_2O\,(l)$	+ 1.69	-489.2

Note in air (O_2)

Reduction to $Mn^{2+}{}_{aq}$ favoured

$O_2 + 2\,Mn^{2+}{}_{aq} + 2\,H_2O \rightleftharpoons 2\,MnO_2(s) + 4\,H^+{}_{aq}$	0.0	0

pH = 14

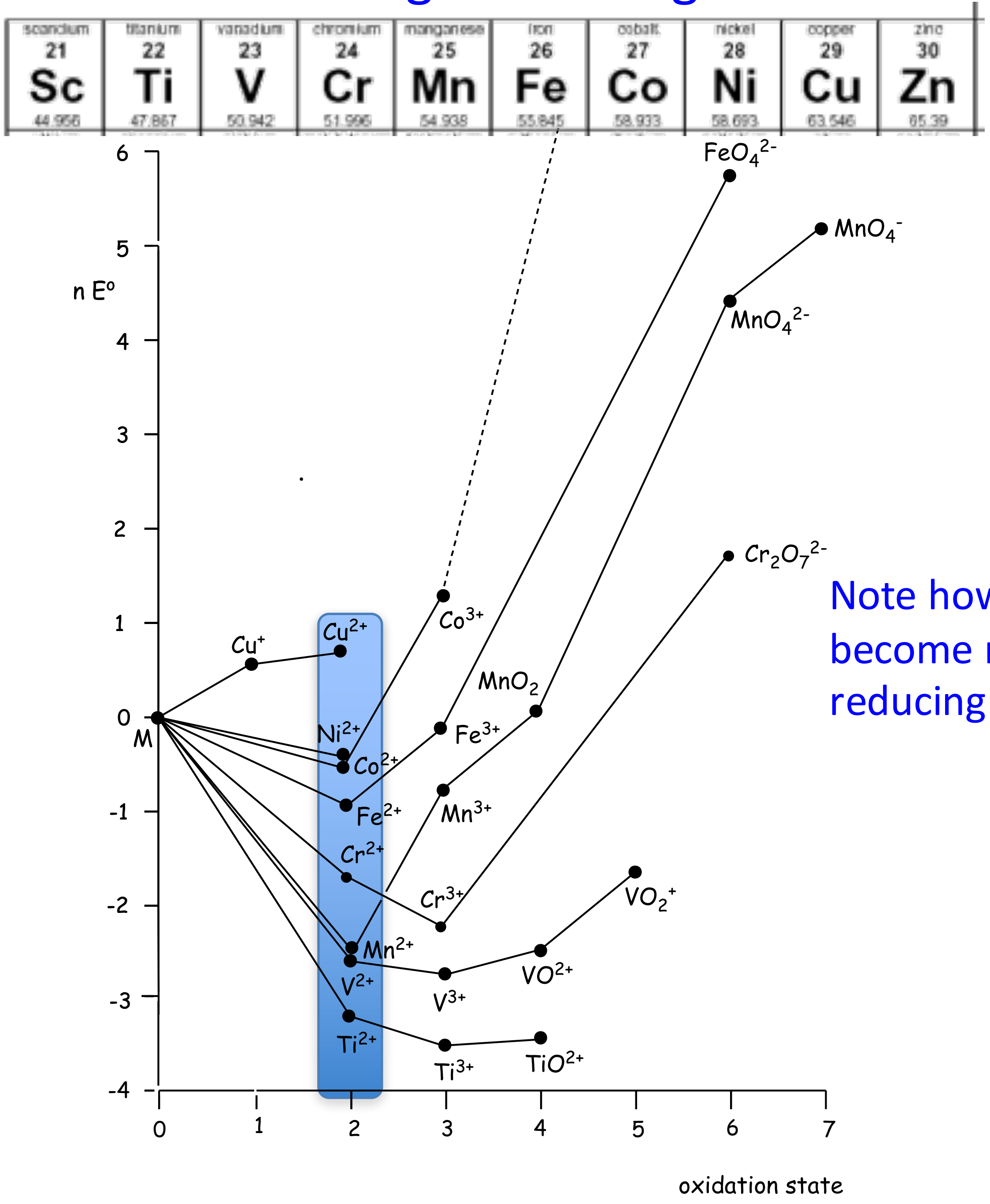
$MnO_4^-{}_{aq} + 4\,H_2O + 5\,e^- \rightleftharpoons Mn(OH)_2(s) + 6\,OH^-{}_{aq}$	+ 0.34	-164
$MnO_4^-{}_{aq} + 2\,H_2O + 3\,e^- \rightleftharpoons MnO_2(s) + 4\,OH^-{}_{aq}$	+ 0.59	-170.8

Note in air (O_2)

Reduction to MnO_2 favoured

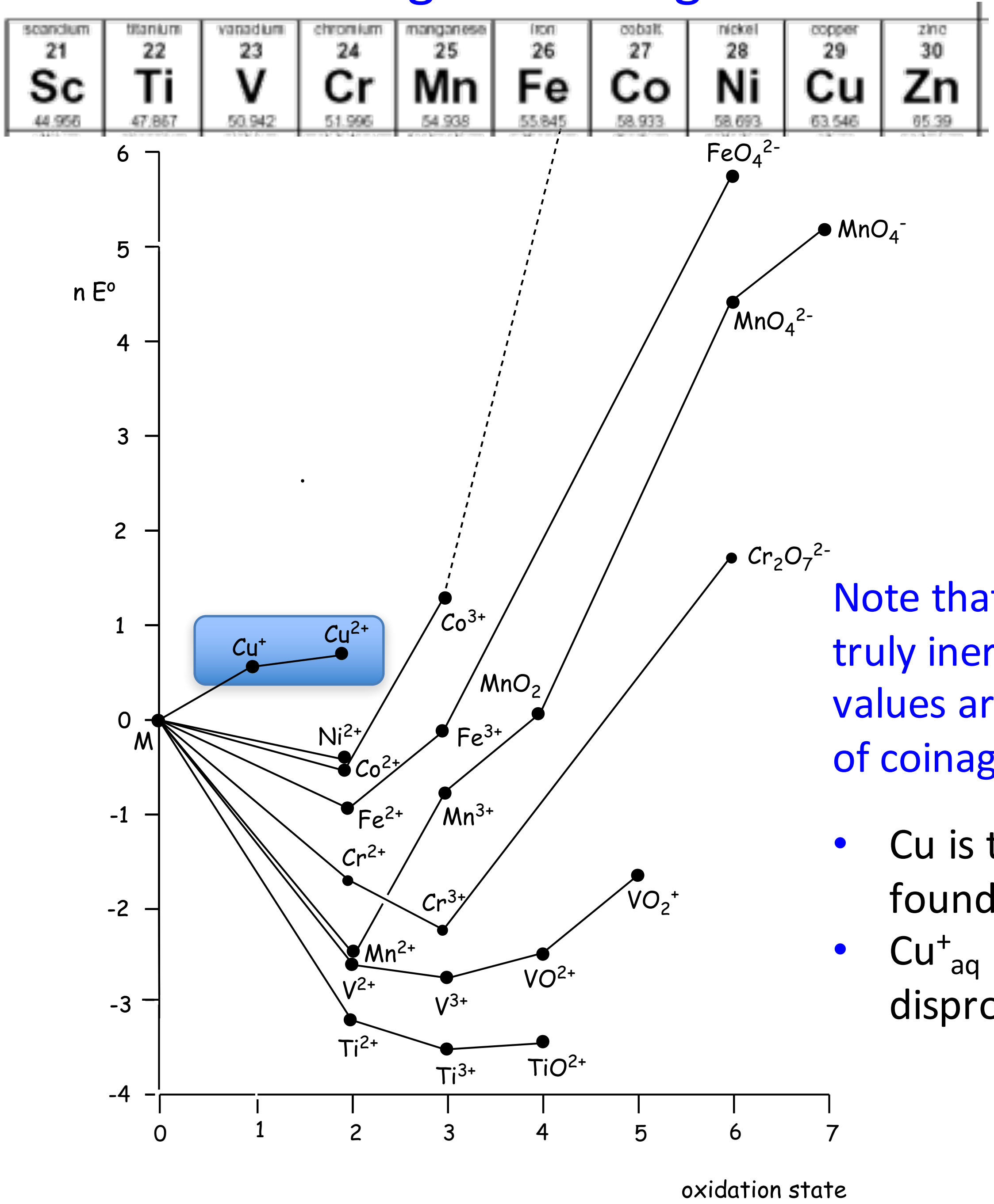
$O_2 + 2\,Mn(OH)_2(s) \rightleftharpoons 2\,MnO_2(s) + 2\,H_2O$	+ 0.44	-169.8

Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams along the 3d Series



Note how the lower states become more stable and less reducing along the period

Quantification of Oxidizing and Reducing Strengths
Frost-Ebsworth Diagrams along the 3d Series



Note that copper is the first truly inert 3d metal (all E° values are positive – typical of coinage metals

- Cu is the only 3d metal found naturally
- Cu^+_{aq} is unstable WRT disproportionation

Quantification of Oxidizing and Reducing Strengths

$$M^{2+}_{aq} + 2\,e^- \rightleftharpoons M(s)$$

consists of the three processes:

$$M(s) \longrightarrow M(g) \quad \text{atomization} \quad H^o_a$$

$$M(g) \longrightarrow M^{2+}(g) \quad \text{ionization} \quad (IP_1 + IP_2)$$

$$M^{2+}(g) \longrightarrow M^{2+}_{aq} \quad \text{hydration} \quad H^o_{hyd}$$

University of St Andrews

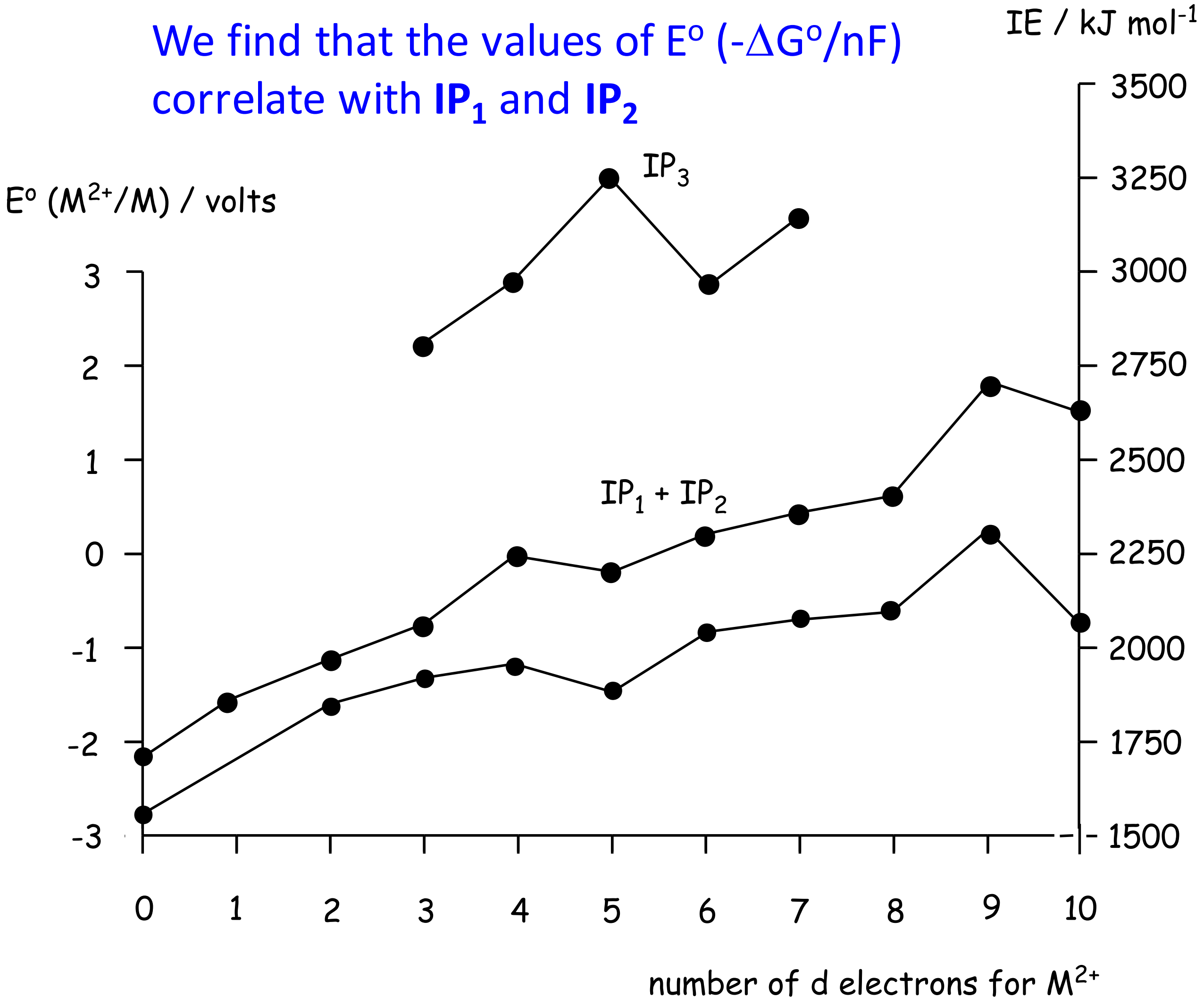
CH3514

Quantification of Oxidizing and Reducing Strengths

$$M^{2+}_{aq} + 2\,e^- \rightleftharpoons M(s)$$

Do any of the trends in E° values correlate any of these processes? **YES**

We find that the values of E° (-ΔG°/nF) correlate with **IP_1** and **IP_2**

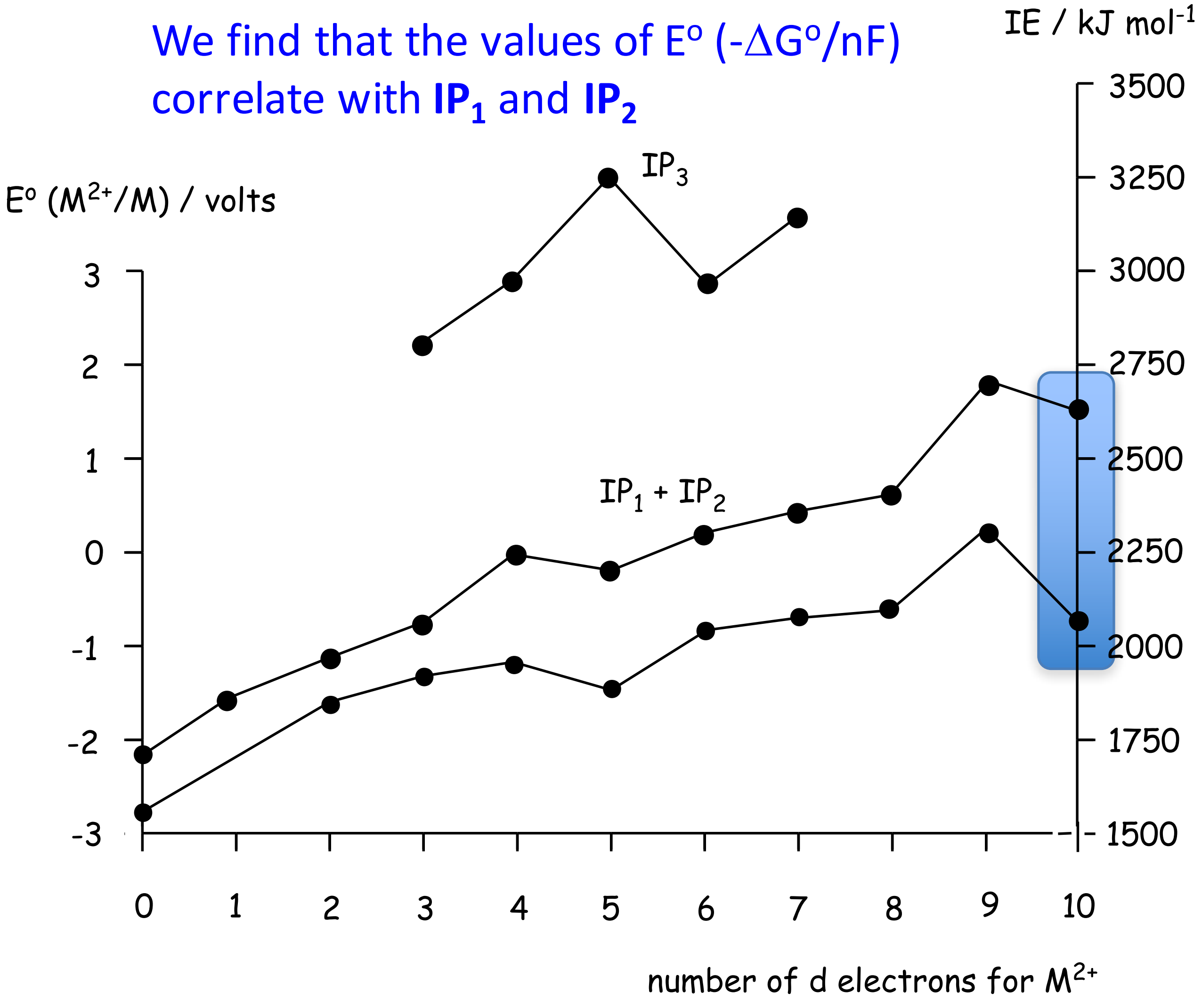


Quantification of Oxidizing and Reducing Strengths

The expected variation of ΔH^o_{hyd} with LFSE (forming the aqua complexes) does not contribute significantly.

The low E° for Zn^{2+}/Zn does correlate however with an unusually low value of ΔH^o_a for Zn(s)

We find that the values of E° (-ΔG°/nF) correlate with **IP_1** and **IP_2**

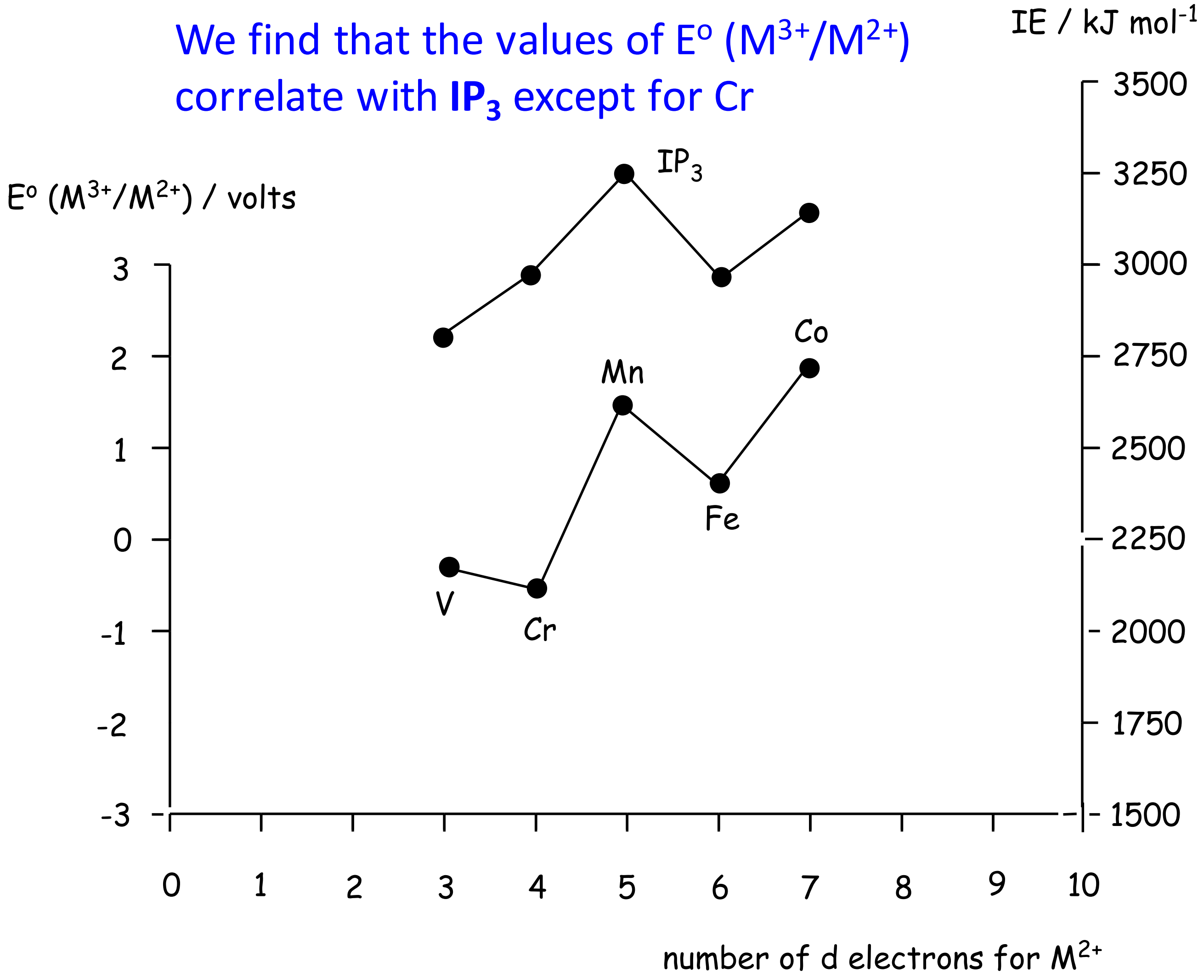


Quantification of Oxidizing and Reducing Strengths

Furthermore, $E^o(M^{3+}/M^{2+})$ correlates with IP_3

Once again the variation in respective ΔH^o_{hyd} values of M^{2+} and M^{3+} is not significant

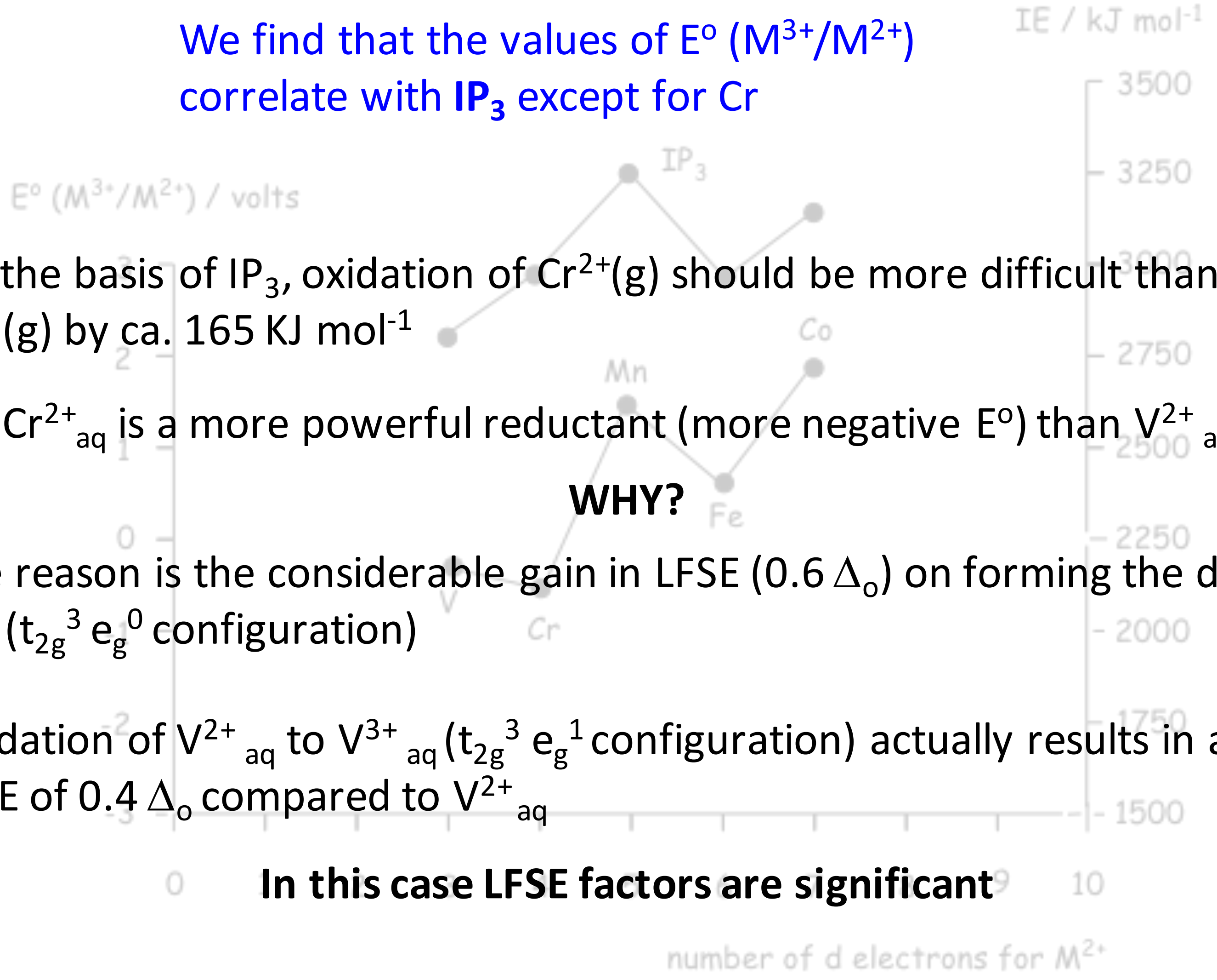
We find that the values of E^o (M^{3+}/M^{2+}) correlate with **IP_3** except for Cr



Quantification of Oxidizing and Reducing Strengths

Furthermore, E^o(M^{3+}/M^{2+}) correlates with IP_3

Once again the variation in respective ΔH^o_{hyd} values of M^{2+} and M^{3+} is not significant



We find that the values of E^o (M^{3+}/M^{2+}) correlate with **IP_3** except for Cr

On the basis of IP_3, oxidation of Cr^{2+}(g) should be more difficult than with V^{2+} (g) by ca. 165 KJ mol^{-1}

Yet Cr^{2+}_{aq} is a more powerful reductant (more negative E^o) than V^{2+}_{aq}

WHY?

The reason is the considerable gain in LFSE (0.6 Δ_o) on forming the d^3 Cr^{3+} ion (t_{2g}^3 e_g^0 configuration)

Oxidation of V^{2+}_{aq} to V^{3+}_{aq} (t_{2g}^3 e_g^1 configuration) actually results in a loss of LFSE of 0.4 Δ_o compared to V^{2+}_{aq}

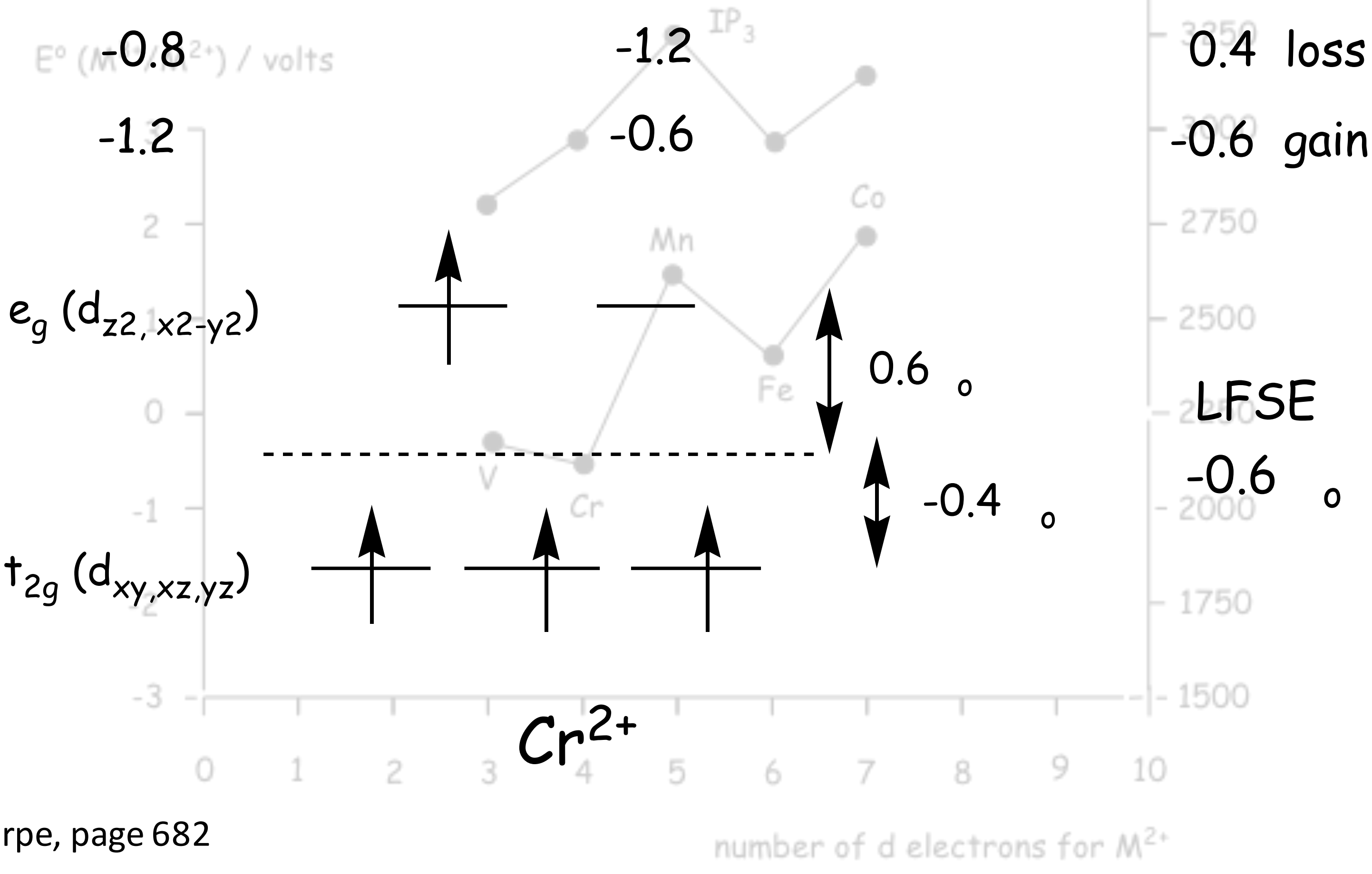
In this case LFSE factors are significant

Quantification of Oxidizing and Reducing Strengths

Furthermore, $E^o(M^{3+}/M^{2+})$ correlates with IP_3

Once again the variation in respective ΔH^o_{hyd} values of M^{2+} and M^{3+} is not significant

M	M^{3+} LFSE units of o	M^{2+} LFSE units of o	Change in LFSE M^{2+}->M^{3+} units of o
V	-0.8	-1.2	0.4 loss
Cr	-1.2	-0.6	-0.6 gain

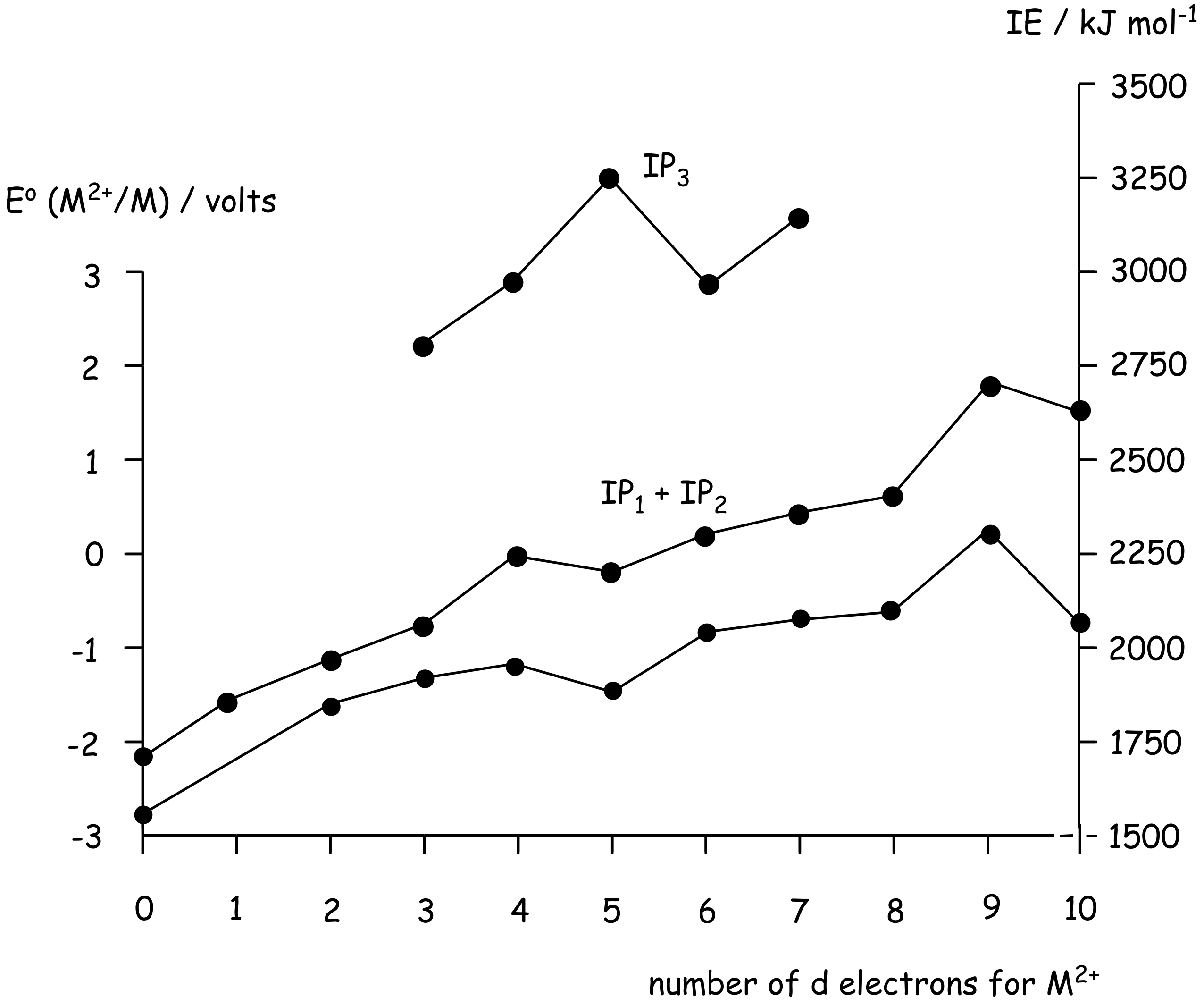


Housecroft and Sharpe, page 682

Quantification of Oxidizing and Reducing Strengths

In summary, E° values in solution largely correlate with the relevant ionization potential, IP_n

Only in certain extreme cases do LFSE factors play a significant part *e.g.*, $Cr^{2+}_{aq}/Cr^{3+}_{aq}$

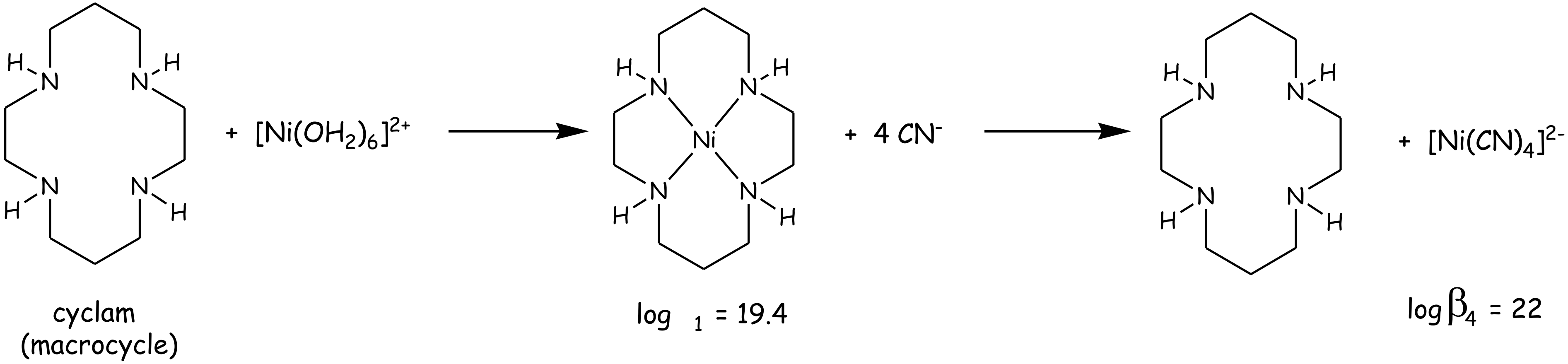


Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Kinetics versus thermodynamics – do they correlate?

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Consider the following process:



$$[Ni(OH_2)_6]^{2+} \quad + \quad 4\ CN^- \xrightleftharpoons{\log\beta_4} [Ni(CN)_4]^{2-} \quad + \quad 6\ H_2O \qquad \log\ _4 = \ 22$$

This is one of the largest log β_n values known for a monodentate ligand replacing H_2O

What this means is that $[Ni(CN)_4]^{2-}$ is very stable thermodynamically

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Consider the rate of the reaction for the following process:

$$[Ni(CN)_4]^{2-} \quad + \quad {}^*CN^- \quad \xrightarrow{k} \quad [Ni({}^*CN)(CN)_3]^{2-} \quad + \quad CN^-$$

exchange of CN^- ligand

$$k = 2.3 \times 10^6 \ M^{-1} \ s^{-1}$$

- representing an exchange event every microsecond!!!

What this means is that $[Ni(CN)_4]^{2-}$ is very **labile**!

These experiments show that **thermodynamic stability** does not necessarily correlate with **kinetic inertness**

The attainment of equilibrium in metal ion complexation processes can be an extremely fast process; irrespective of the size of the stability constants: K_n or β_n

In fact ms and μs timescale ligand exchange events involving monodentate ligands are common within 3d transition metal complexes

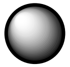
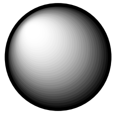
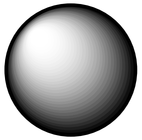
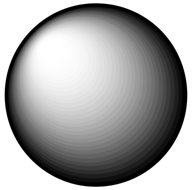
Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

A wide range of rates is relevant for ligand exchange reactions at metal complexes

Consider water exchange on the aqua species

For main group metal ions these range from the most labile (Cs^+_{aq}, half life = 1 ns) to the most inert (Al^{3+}_{aq}, half life = 1 s) - 9 orders of magnitude

This is mostly as a result of variations in the metal ionic radius which affects the strength of the predominantly ionic (electrostatic) bonding to the coordinated waters

	Group 2 aqua ions	Ionic radius / pm	Water exchange half life / s
	$[Be(OH_2)_4]^{2+}$	27	10^{-2}
	$[Mg(OH_2)_6]^{2+}$	72	10^{-5}
	$[Ca(OH_2)_7]^{2+}$	105	10^{-7}
	$[Ba(OH_2)_8]^{2+}$	142	10^{-9}

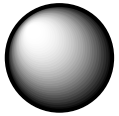
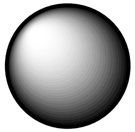
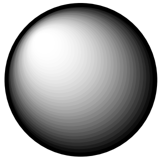
Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

A wide range of rates is relevant for ligand exchange reactions at metal complexes

Consider water exchange on the aqua species

For main group metal ions these range from the most labile (Cs^+_{aq}, half life = 1 ns) to the most inert (Al^{3+}_{aq}, half life = 1 s) - 9 orders of magnitude

This is mostly as a result of variations in the metal ionic radius which affects the strength of the predominantly ionic (electrostatic) bonding to the coordinated waters

	Group 13 aqua ions	Ionic radius / pm	Water exchange half life / s
	$[Al(OH_2)_6]^{3+}$	54	1
	$[Ga(OH_2)_6]^{3+}$	62	10^{-3}
	$[In(OH_2)_6]^{3+}$	80	10^{-6}

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

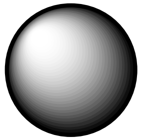
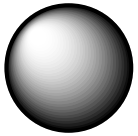
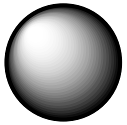
A wide range of rates is relevant for ligand exchange reactions at metal complexes

Consider water exchange on the aqua species

However for the 3d transition metal ions **size is not the only factor**

Here there is no correlation with size V^{2+} has the largest radius but it is the most inert

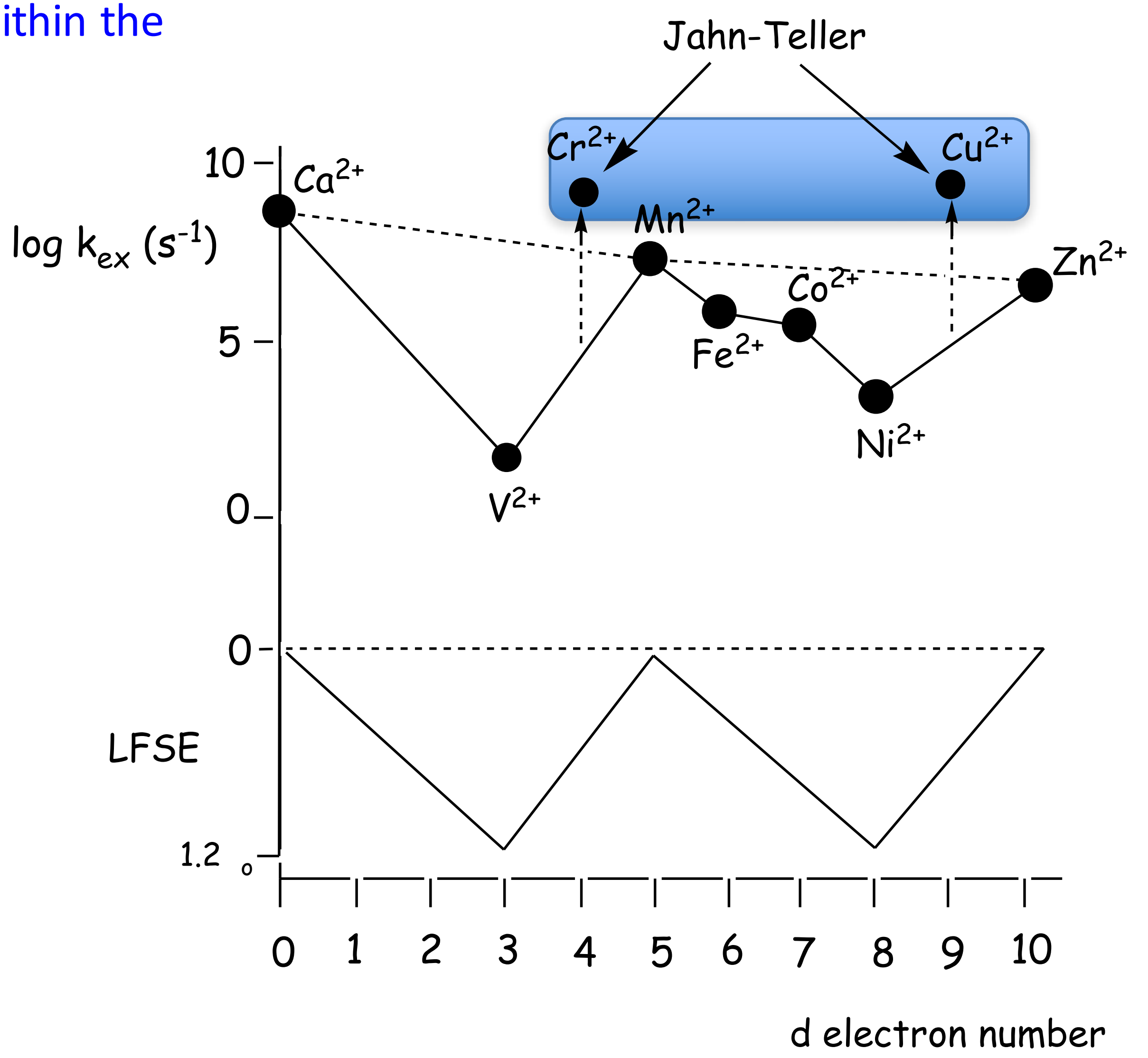
The half lives (**rates**) of exchange, just like the stability constants we saw earlier, **correlate** with **LFSE** not size

	3d aqua ions	Ionic radius / pm	Water exchange half life / s
	$[V(OH_2)_6]^{2+}$	79	10^{-2}
	$[Co(OH_2)_6]^{2+}$	75	10^{-6}
	$[Ni(OH_2)_6]^{2+}$	69	10^{-4}

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Values of log k_{ex} (water exchange) for M^{2+} ions along the 3d series

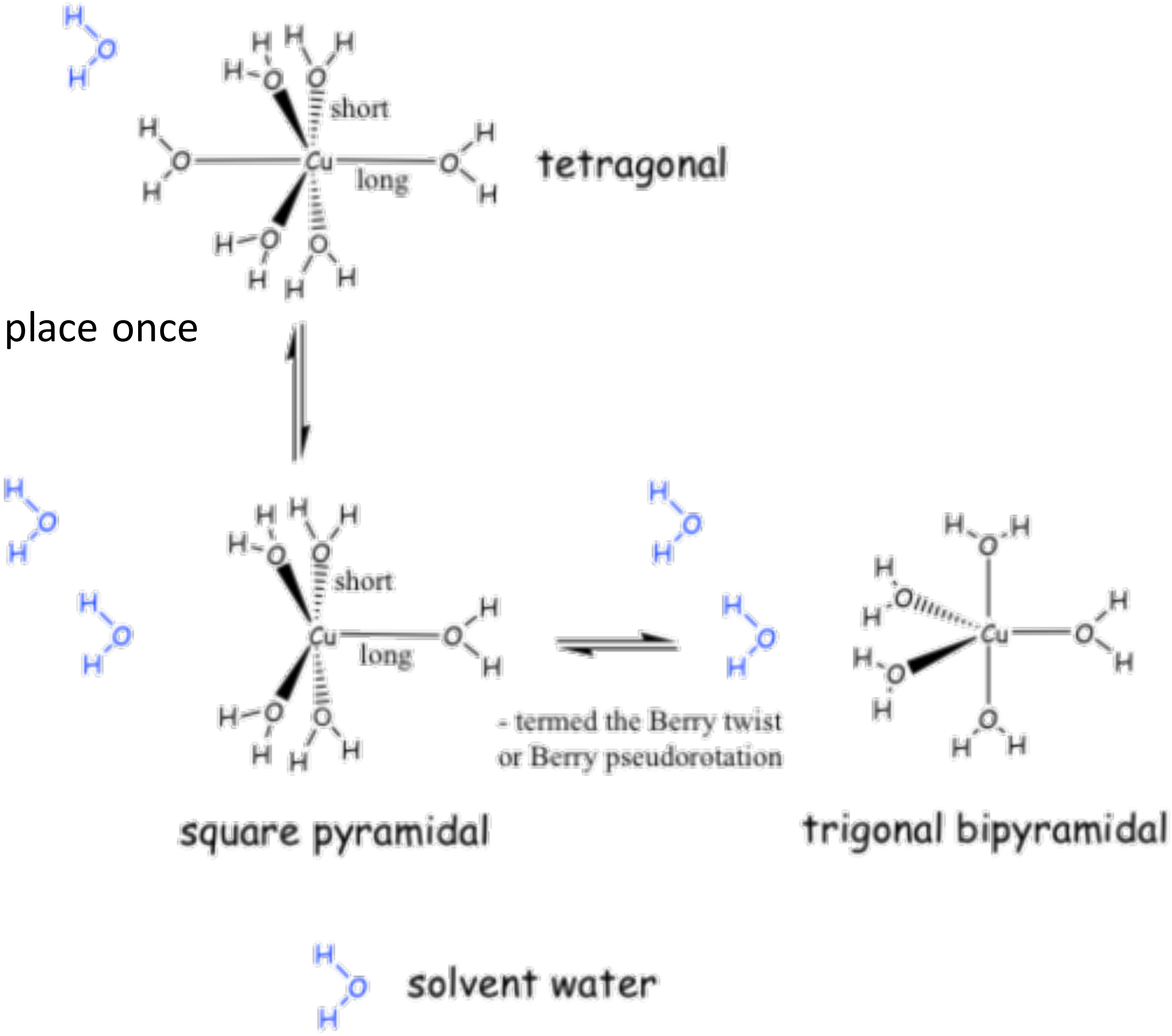
The anomalously high rates for Cr^{2+}_{aq} and Cu^{2+}_{aq} reflect the rapid dynamics attached to the weakly-bonded water ligands within the Jahn-Teller distorted structures



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

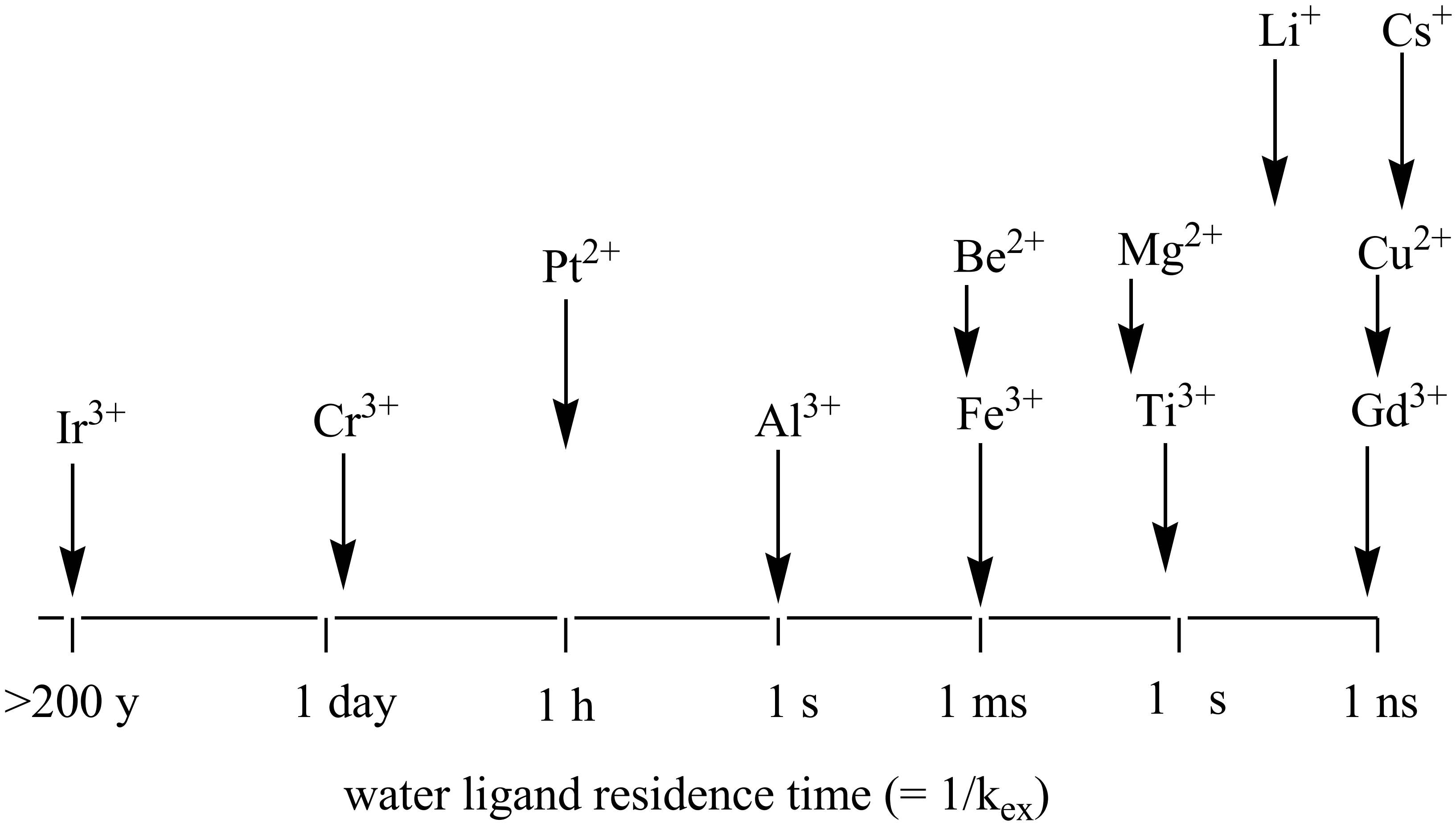
The Jahn-Teller assister fast exchange process on $Cu^{2+}{}_{aq}$

Entire process takes place once every nanosecond!!



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

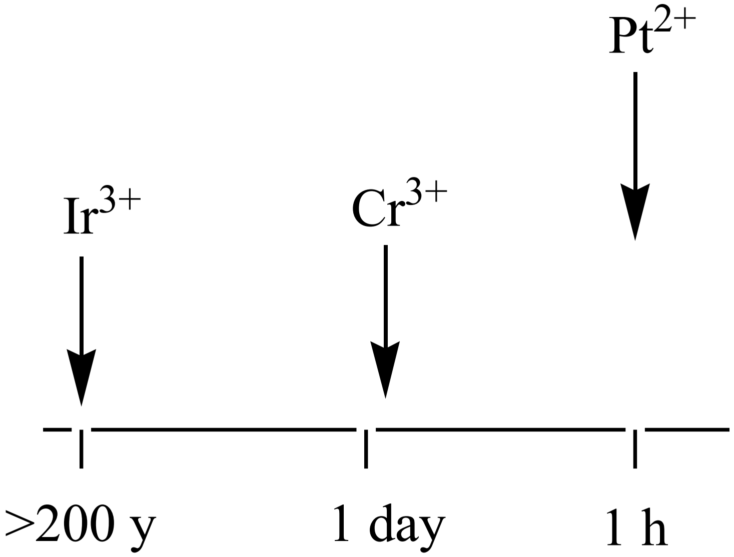
Amazingly, the rates of water ligand exchange on aqua metal ions across the periodic table cover 20 orders of magnitude



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Amazingly, the rates of water ligand exchange on aqua metal ions across the periodic table cover 20 orders of magnitude

Generally,
Lower charge: faster; Higher charge: slower
Larger size: faster; smaller size: slower



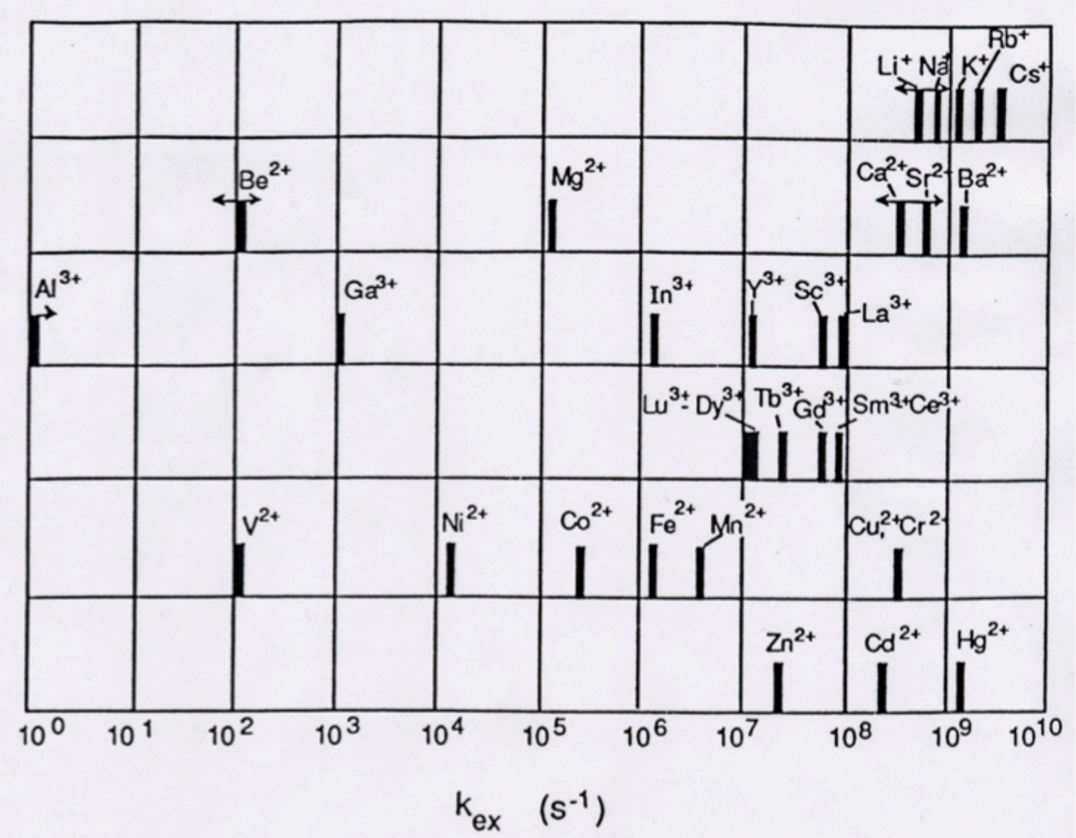


Figure 1.9 Solvent exchange rates for inner-sphere water molecules in M^{n+} (aq). [Adapted from H. Diebler et al., *Pure Appl. Chem.*, *20*, 93–115 (1969).]

water ligand residence time (= $1/k_{ex}$)

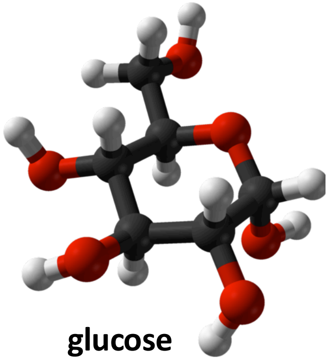
Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Amazingly, the rates of water ligand exchange on aqua metal ions across the periodic table cover <u>20</u> orders of magnitude

Let's put this into perspective

crayon

	average time interval at 25°C before water exchange event
On $Cu^{2+}{}_{aq}$	1 ns – 10^{-9} s
On $Al^{3+}{}_{aq}$	0.1 s – 10^{-1} s
On $Cr^{3+}{}_{aq}$	1 day – 86 400 s
On $Ir^{3+}{}_{aq}$	50 years – 1.58×10^{9} s



glucose

~40% from the Earth to Moon

~ St Andrews to Edinburgh

Could envisage studying the exchange on $Cr^{3+}{}_{aq}$ without problem but what about that on $Ir^{3+}{}_{aq}$?

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

So how was the exchange on $Ir^{3+}{}_{aq}$ measured ?

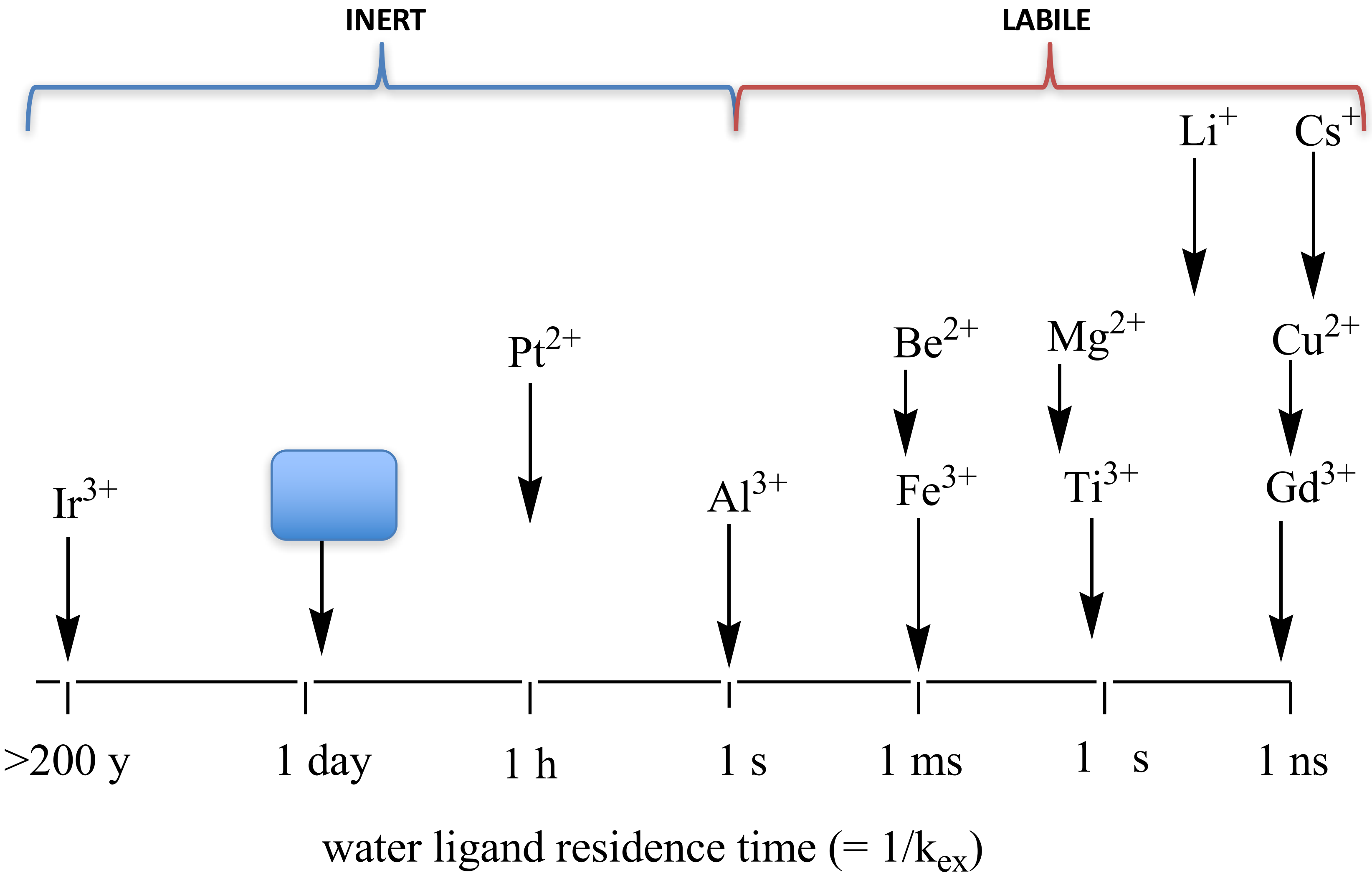
Since water exchange involves bond breaking from M^{n+} to resident water, which has an endothermic activation barrier of about 130 kJ mol^{-1}, raising the temperature will speed up the reaction

water exchange on $[Ir(H_2O)_6]^{3+}$ was studied in pressurized vessels at 120°C – an event occurs now in less than 1 hour – we can follow by NMR using enriched ^{17}O-labelled water (^{17}O has an NMR signal like ^{1}H)

Classification for exchange reactions on metal ions	
τ < 1 min	labile
τ > 1 min	inert

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

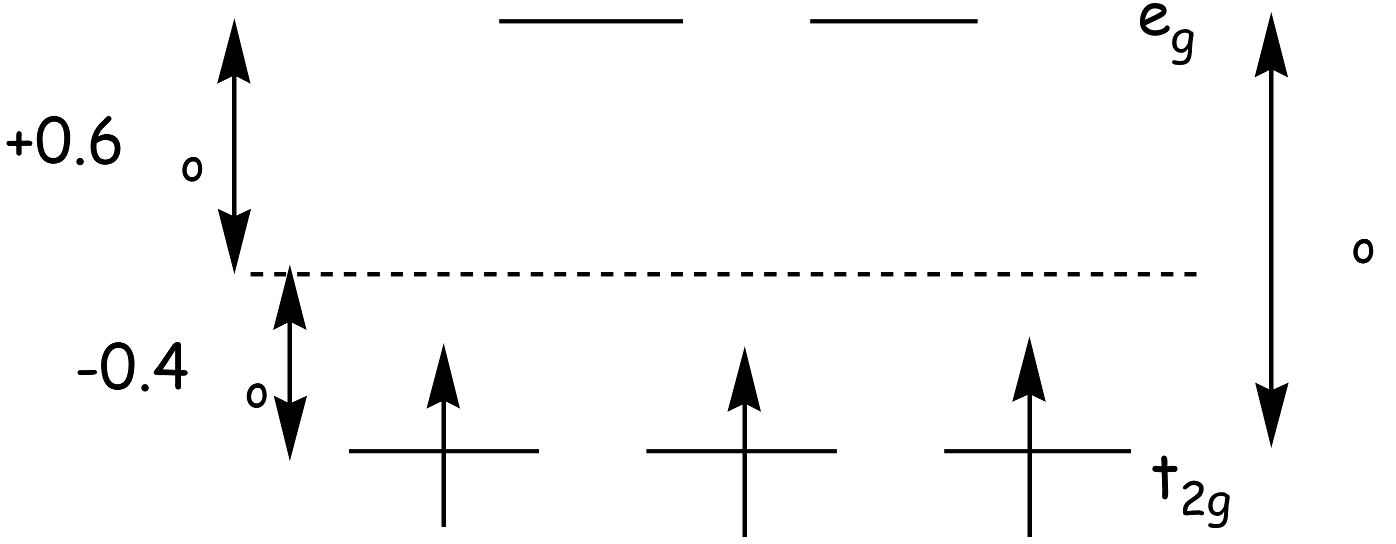
Of all the 3d transition metal aqua ions only **Cr^{3+}_{aq}** is classed as inert – why?



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Of all the 3d transition metal aqua ions only **Cr^{3+}_{aq}** is classed as inert – why?

Octahedral $[Cr(H_2O)_6]^{3+}$ has a high charge coupled with a very stable t_{2g}^3 configuration with $-1.2\Delta_o$ of LFSE

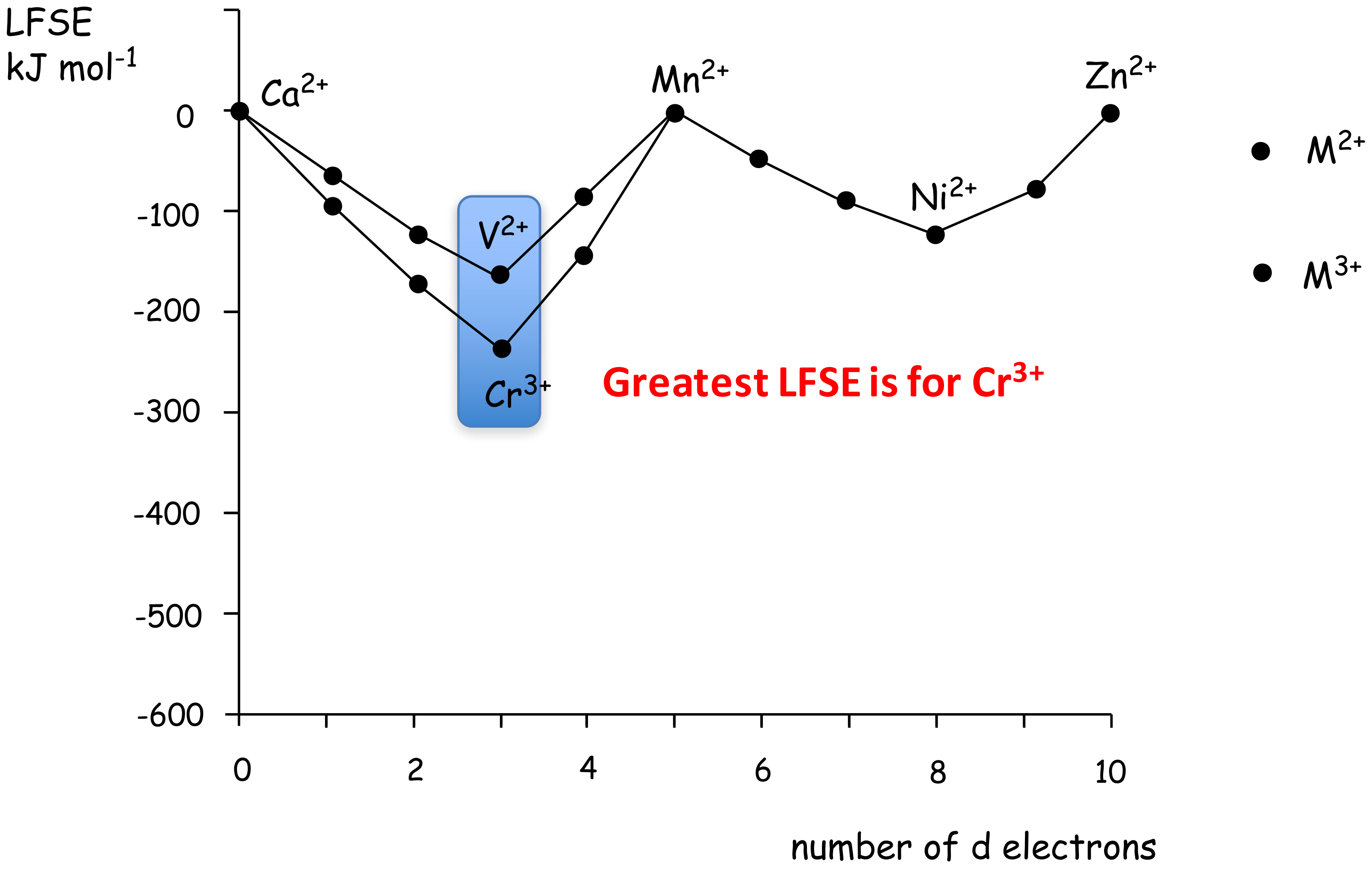


High LFSE correlates with a high ligand field activation energy (LFAE) for exchange

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Of all the 3d transition metal aqua ions only **Cr^{3+}_{aq}** is classed as inert – why?

Octahedral $[Cr(H_2O)_6]^{3+}$ has a high charge coupled with a very stable t_{2g}^3 configuration with $-1.2\Delta_o$ of LFSE

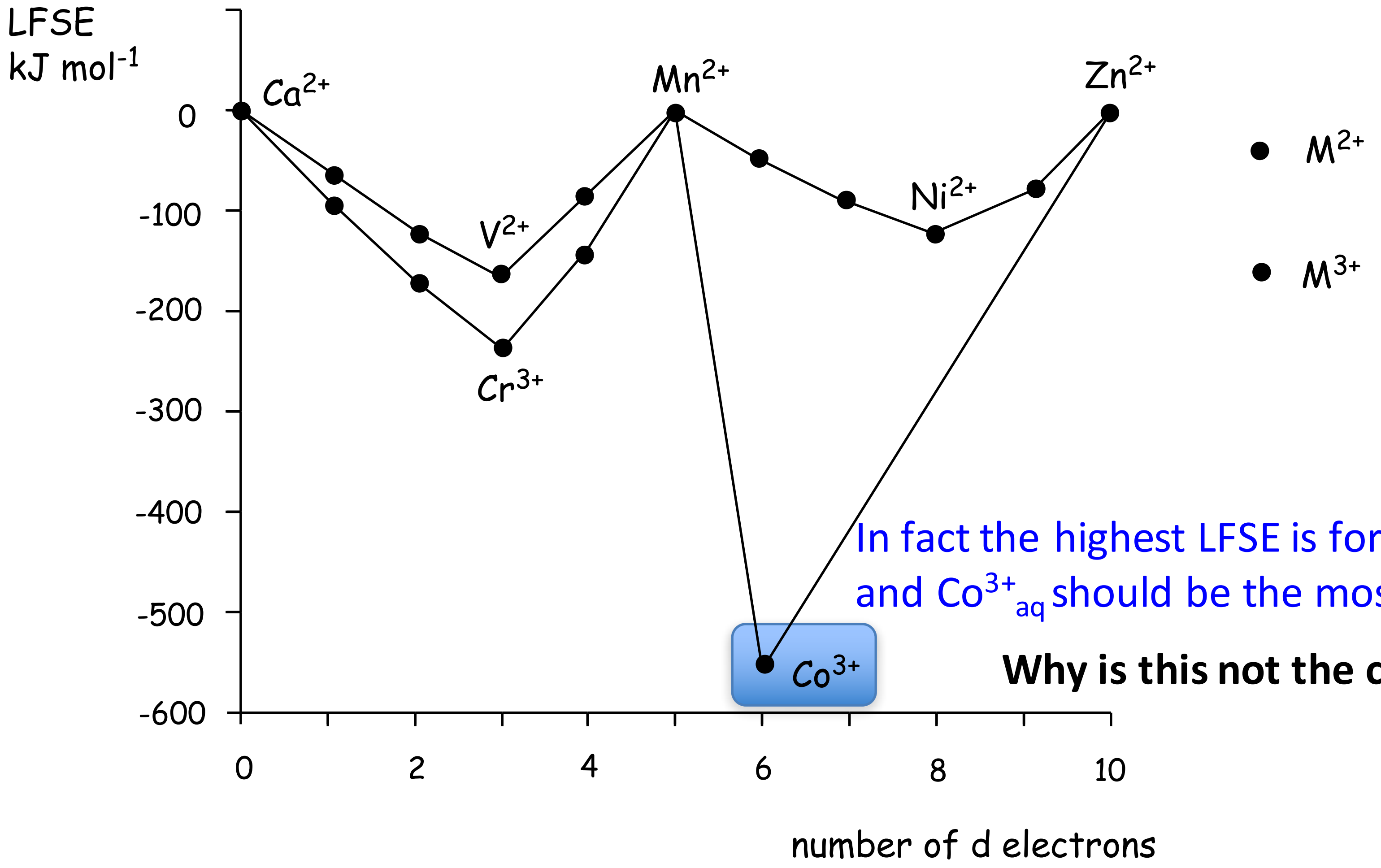


Greatest LFSE is for Cr^{3+}

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Of all the 3d transition metal aqua ions only **Cr^{3+}_{aq}** is classed as inert – why?

Octahedral $[Cr(H_2O)_6]^{3+}$ has a high charge coupled with a very stable t_{2g}^{3} configuration with $-1.2\Delta_o$ of LFSE

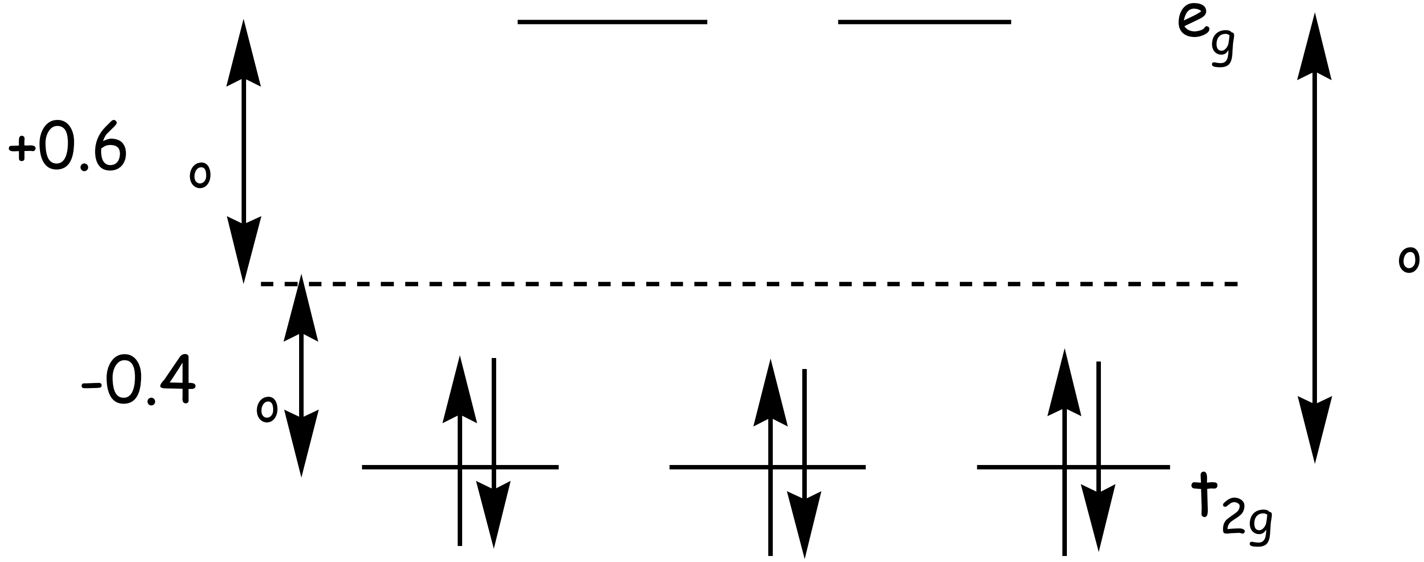


In fact the highest LFSE is for Co^{3+}_{aq} and Co^{3+}_{aq} should be the most inert

Why is this not the case?

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

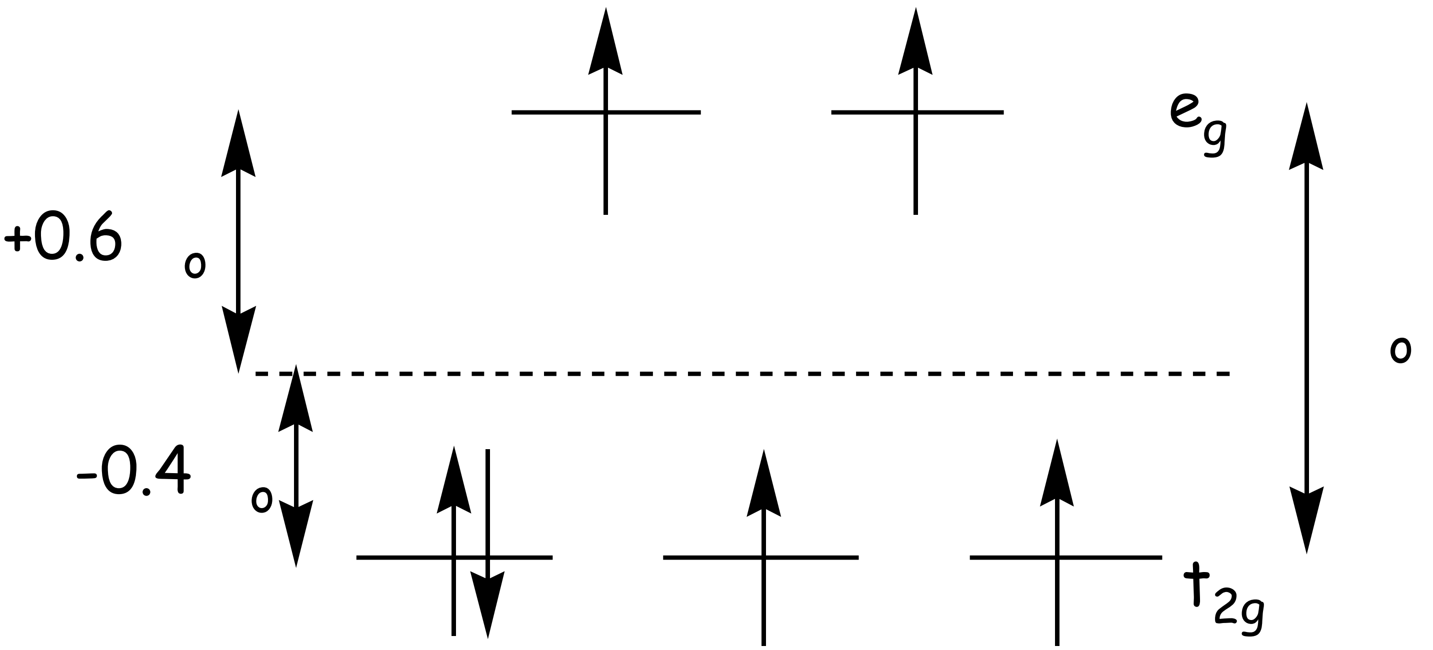
Low spin octahedral $[Co(H_2O)_6]^{3+}$ has a high charge (high Δ_o) coupled with a t_{2g}^6 configuration and therefore has the maximum LFSE possible of $-2.4\Delta_o$



So Co^{3+} has a very high LFAE and should be kinetically inert

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

But how do we know that octahedral $[Co(H_2O)_6]^{3+}$ has a low spin $t_{2g}{}^6$ configuration? The complex could be high spin.



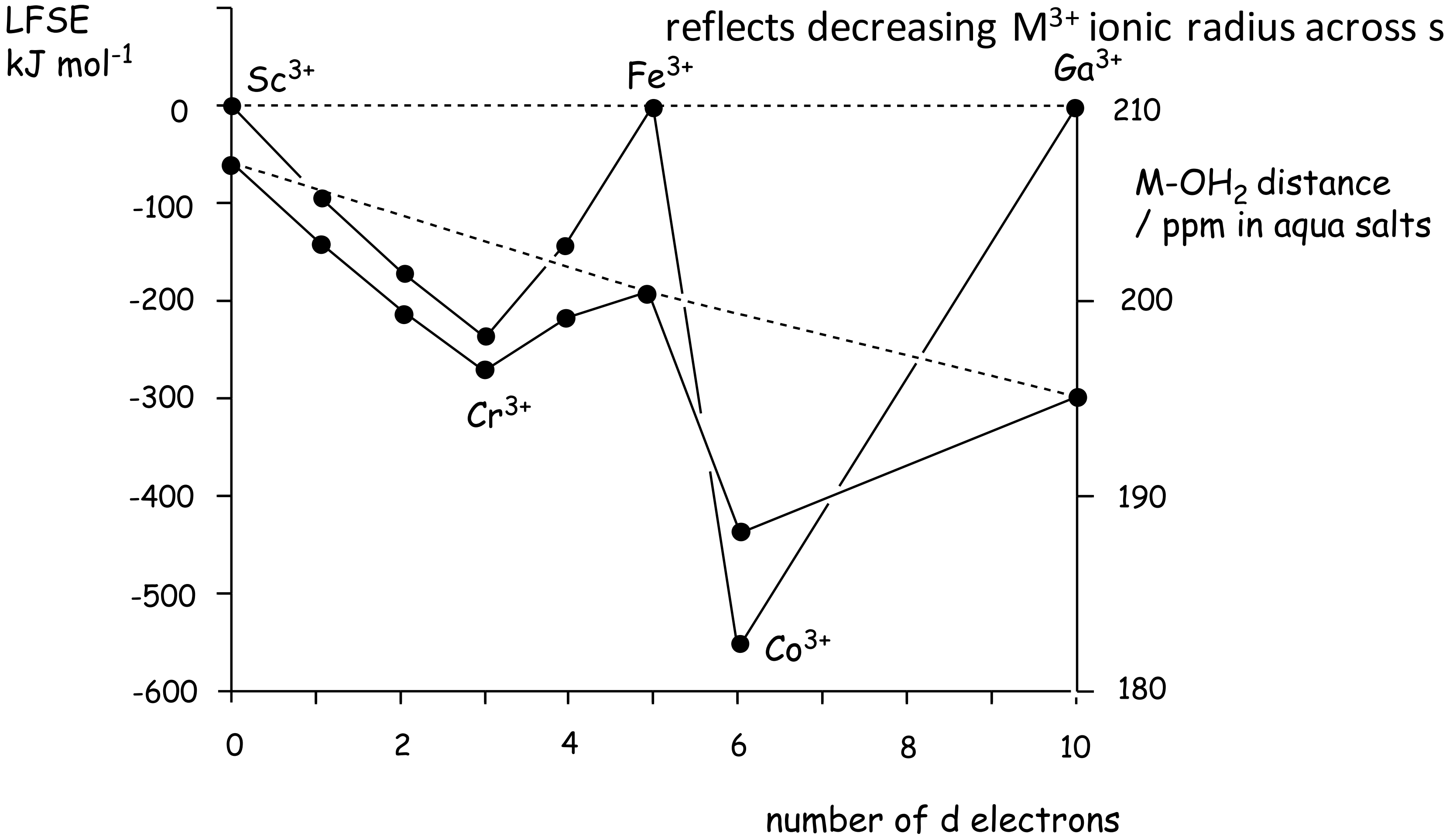
So Co^{3+} would then have a LFSE of only $-0.4\,\Delta_o$

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

So how do we know?

Of course we could look at the magnetic properties but we can also tell from the M-OH_2 distances in the aqua complexes

The decrease in M-OH_2 distance once again reflects decreasing M^{3+} ionic radius across series



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

The rate of exchange on $[Co(OH_2)_6]^{3+}$ has not been measured however because it is **not stable**

$[Co(OH_2)_6]^{3+}$ spontaneously oxidizes water to O_2

$$[Co(OH_2)_6]^{3+} + e^- \rightleftharpoons [Co(OH_2)_6]^{2+} \qquad E^o = +1.98\ V$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^o = +1.23\ V$$

$$\mathbf{\Delta G^o_{cell} = -nFE^o_{cell} = -4*96487*0.75 = -386\ KJ\ mol^{-1}}$$

The exchange reaction observed is catalysed by the more labile $[Co(OH_2)_6]^{2+}$ generated

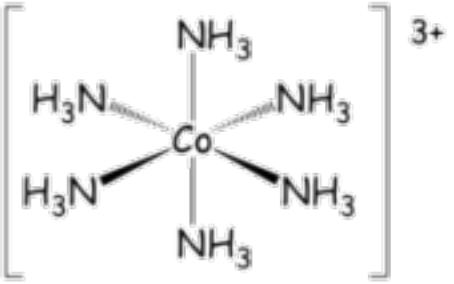
$[Co(OH_2)_6]^{3+}$ provides another good example of the lack of correlation between thermodynamic stability and kinetic lability

$Co(OH_2)_6]^{3+}$ is inert yet only metastable

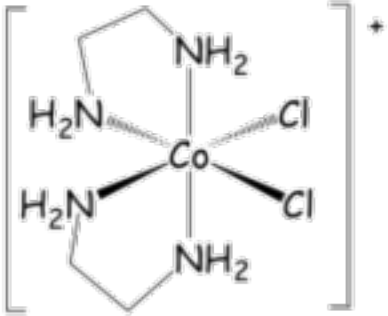
Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Literally hundreds of stable Co^{3+} complexes are known with ligands other than water, most of them N-donor ligands.

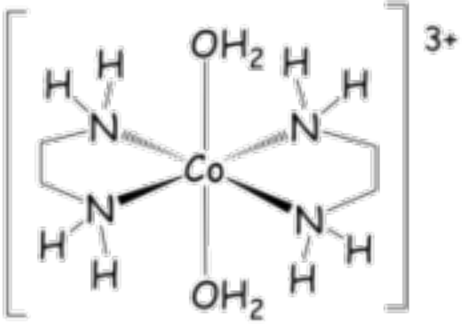
Because of their redox stability, coupled with slow rates of ligand exchange, many of these have played a huge role in developing our understanding of the mechanisms of reactions at transition metal centres



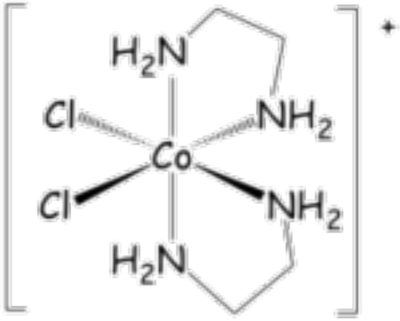
$E^o (Co^{III/II}) = + 0.1$ V



cis - Λ



trans

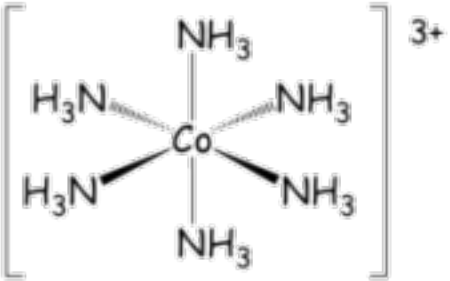


cis - Δ

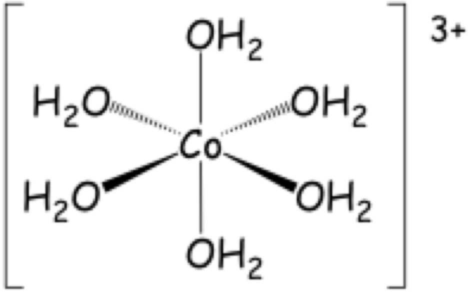
Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Literally hundreds of stable Co^{3+} complexes are known with ligands other than water, most of them N-donor ligands.

Because of their redox stability, coupled with slow rates of ligand exchange, many of these have played a huge role in developing our understanding of the mechanisms of reactions at transition metal centre



$E^o (Co^{III/II}) = + 0.1$ V

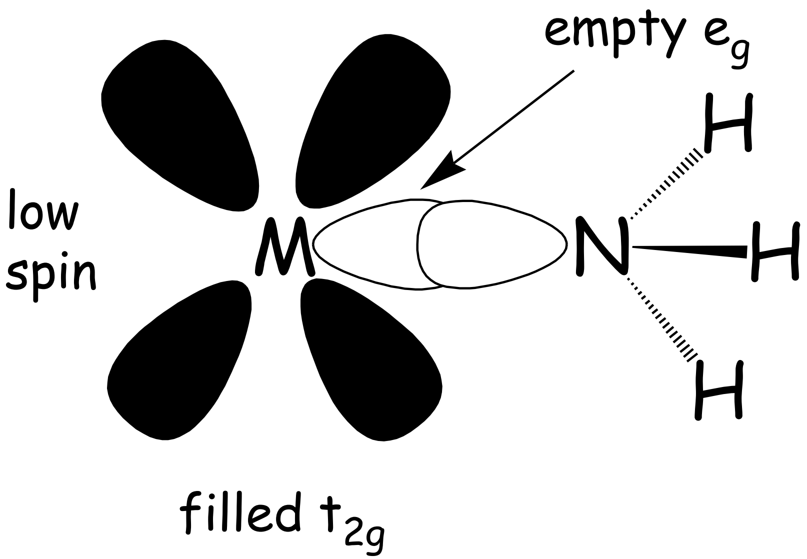


$E^o (Co^{III/II}) = + 1.98$ V

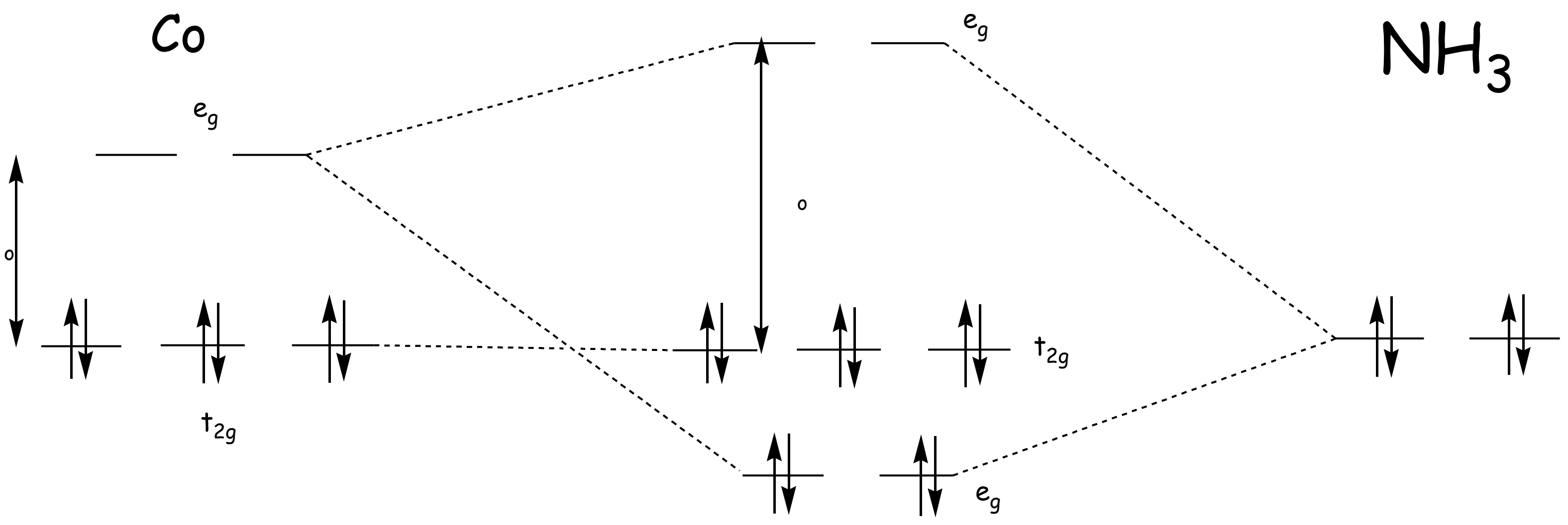
Why this huge difference in E^o values ?
with Co^{III} stabilized hugely with N-donors like NH_3

Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Why this huge difference in E° values ?

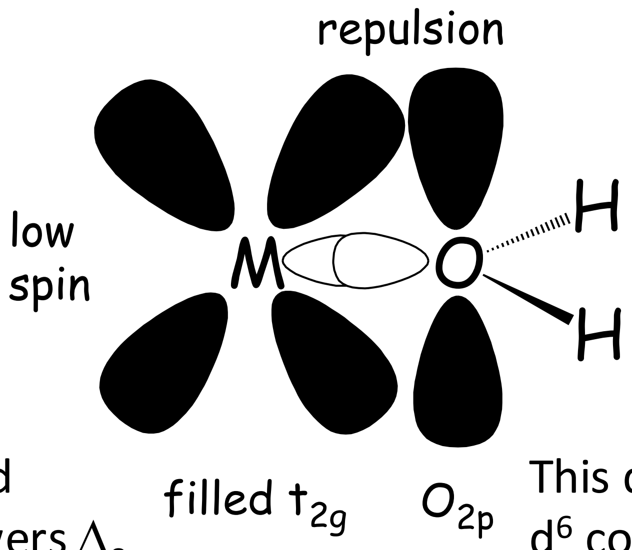


σ-donor ligand



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

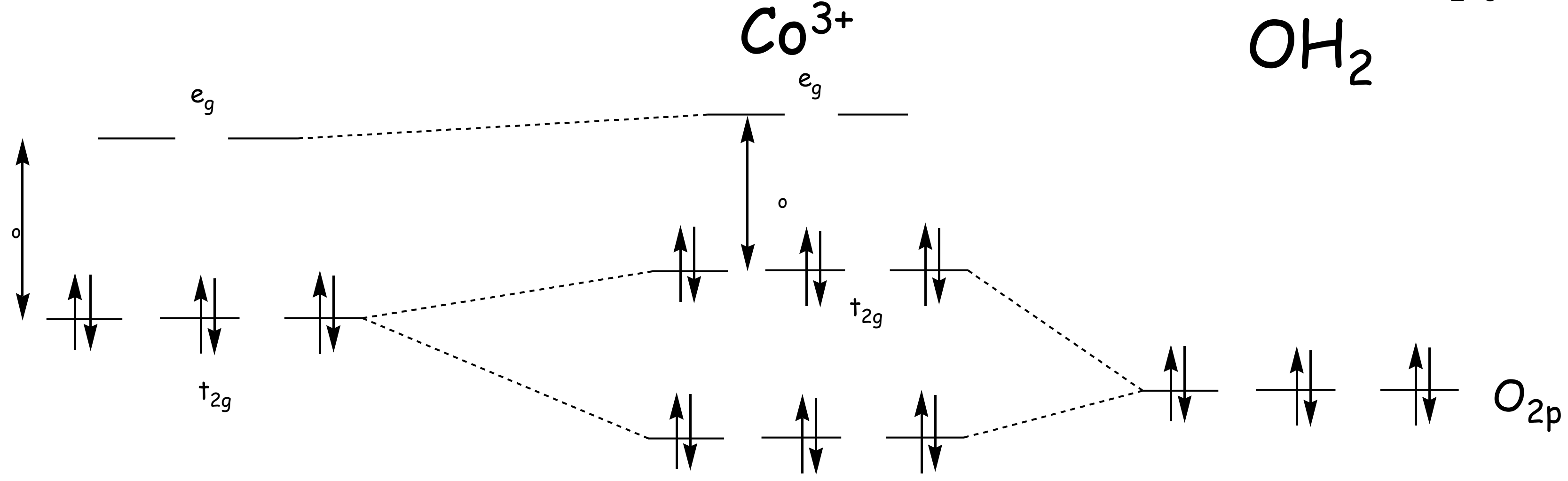
Why this huge difference in E^o values ?



π-donor ligand in addition to σ-donation

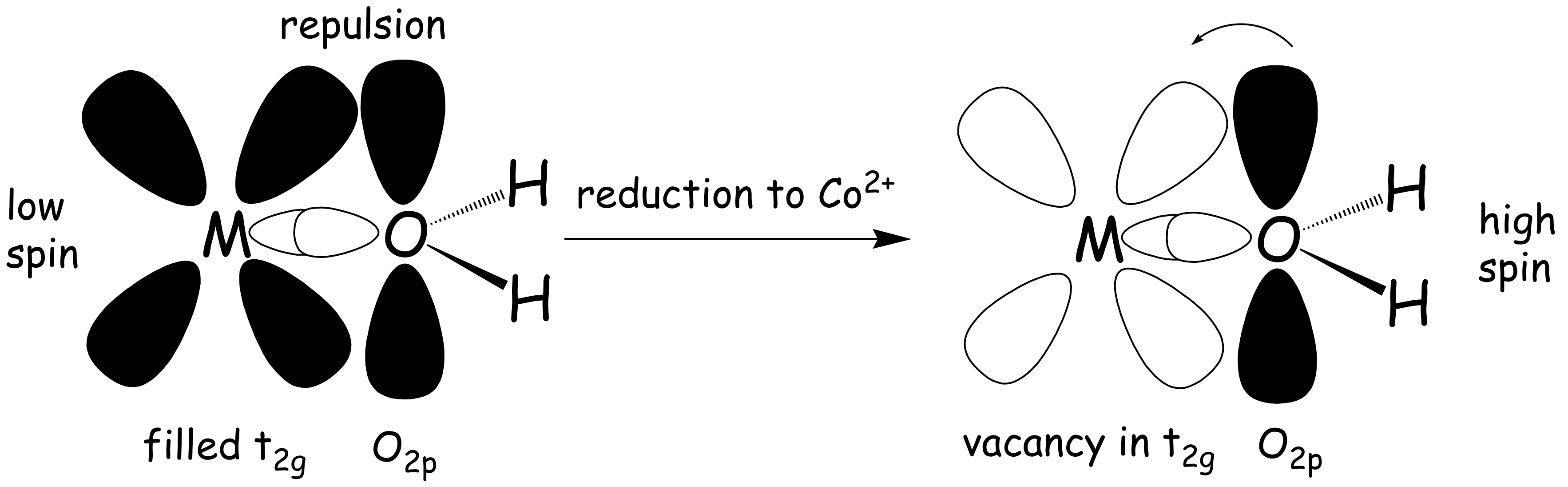
Stronger π-donation coupled with weaker σ-donation lowers Δ_o

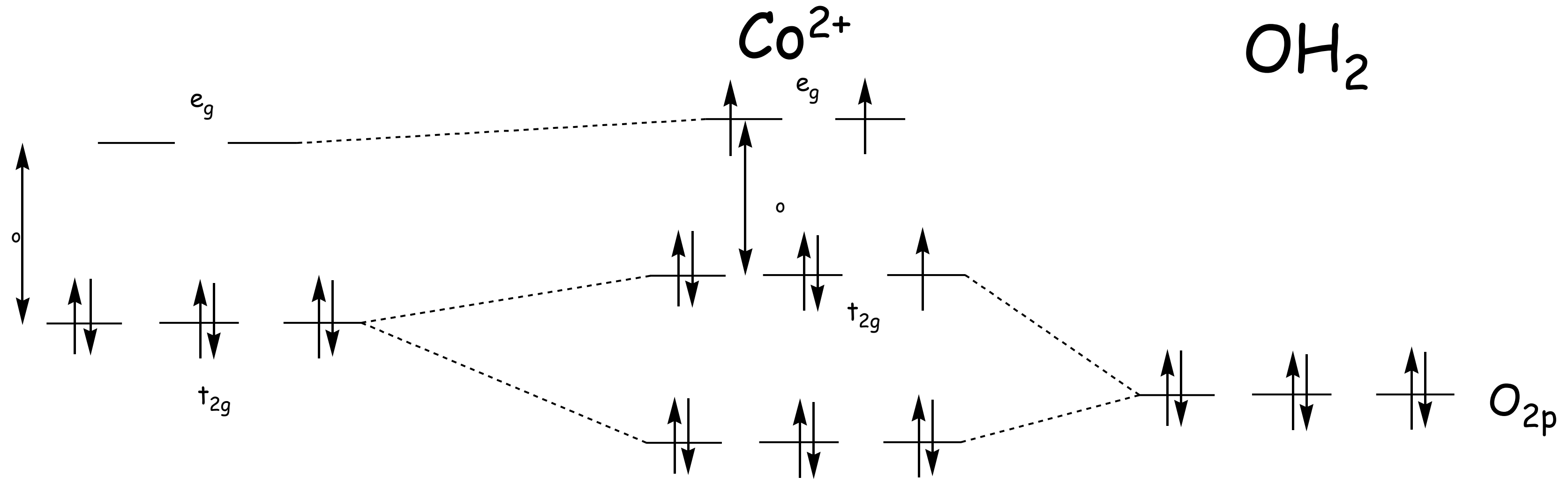
This decreases the stability of the *ls* d^6 configuration with respect to the reduction to the *hs* d^7 $[Co(OH_2)_6]^{2+}$ ($\Delta_o < P$)



Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

Why this huge difference in E° values ?





Rates of Reactions Involving 3d Transition Metal Ions in Aqueous Solution

There are only two known high spin Co^{3+} complexes:

- $[Co(OH_2)_3F_3]$
- $[CoF_6]^{3-}$

This is due to good π-donation from F^-, which dramatically decreases Δ_o

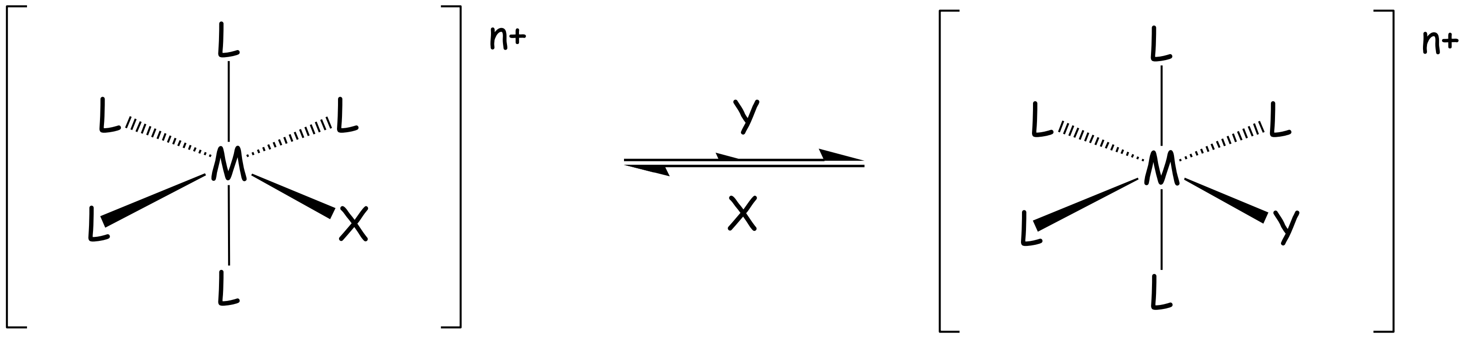
All other Co complexes are low spin, which is due to stronger σ-donation outweighing all other effects

An Introduction to Mechanisms in Organic Chemistry

You all are familiar with substitution reactions on carbon: S_N1 and S_N2

There exists comparable mechanisms of ligand replacement on the metal

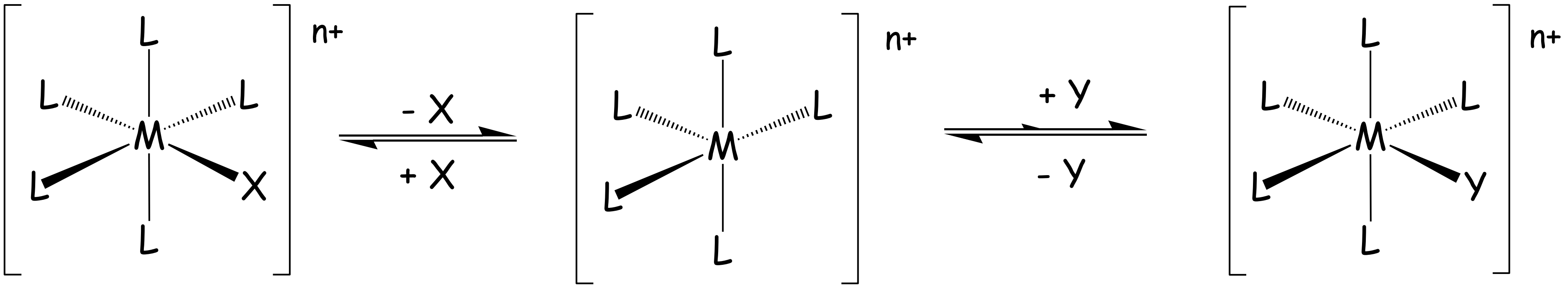
- Dissociative – similar to S_N1
- Associative – similar to S_N2



An Introduction to Mechanisms in Organic Chemistry

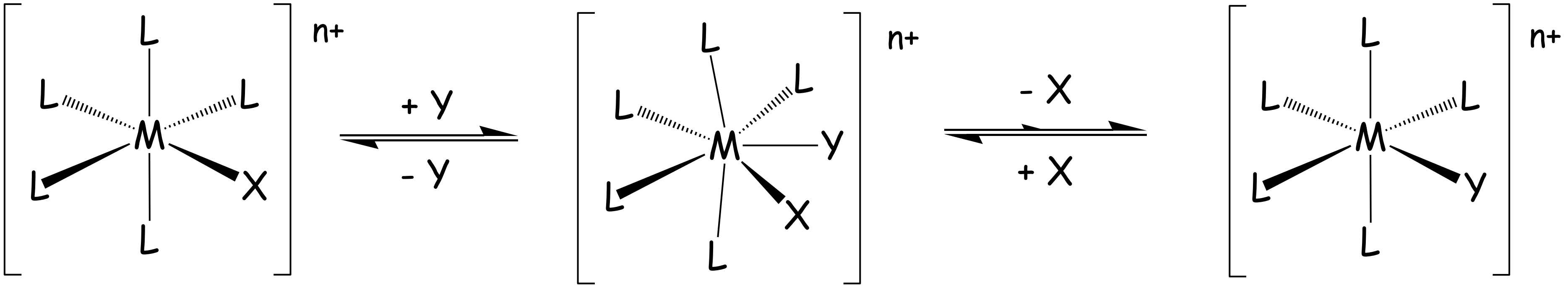
The Dissociative path:

X leaves first and then Y coordinates at the vacant site on the metal



The Associative path:

M-Y bond forms first followed by de-coordination of X



Which path would you predict to have the **largest** activation energy?

Answer: The dissociative path. Why?

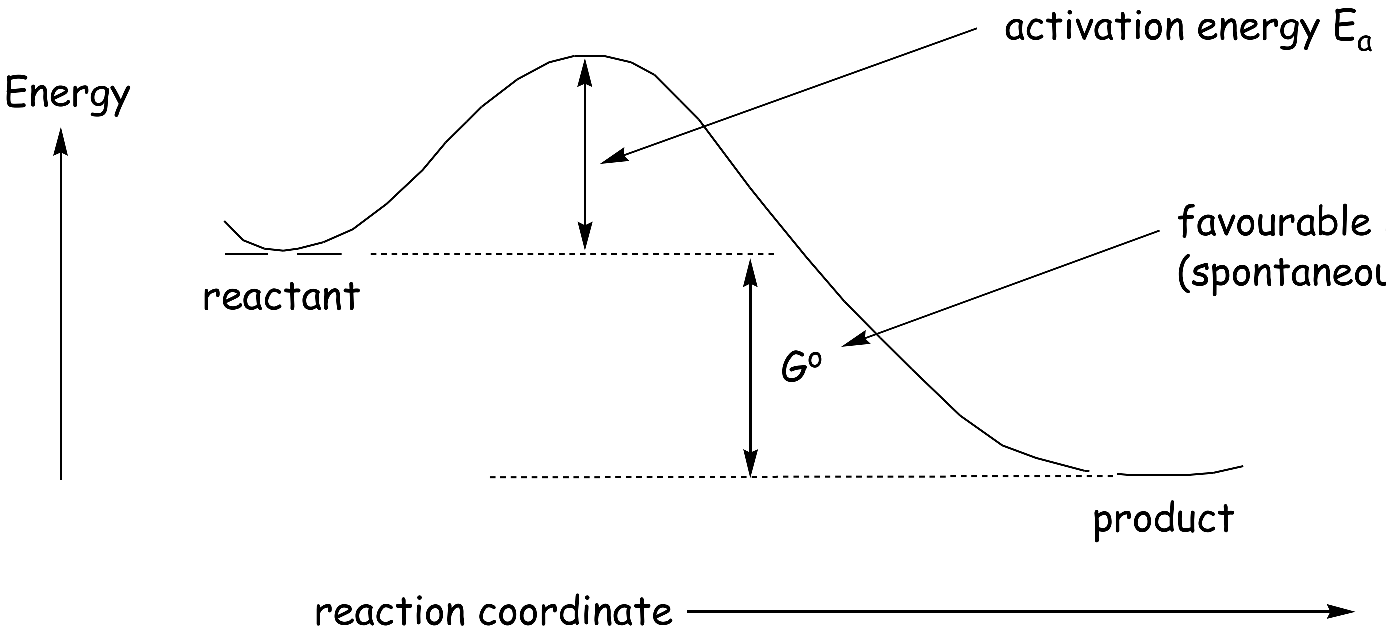
This mechanism involves a bond-breaking step (M-X bond) in the RDS, which will be endothermic before the new bond is formed – formally two step reaction

Similarly, S_N1 reactions are frequently slower than S_N2 reactions for the same reason

The associative path involves a bond-making step (M-Y), which will be exothermic prior to bond breaking (M-X) and so should possess a lower activation energy.

Additionally, the presence of the new M-Y bond may lower to energy required to break the M-X bond

The activation energy E_a can be determined from the temperature dependence of the reaction rate according to the Arrhenius or Eyring equation.



The Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad k = A\,e^{\left(\frac{-E_a}{RT}\right)}$$

The Eyring equation:

$$\ln k = \ln\left(\frac{k'\,T}{h}\right) - \frac{\Delta G}{RT} \quad \text{or} \quad k = \left(\frac{k'\,T}{h}\right) e^{\left(\frac{\Delta G}{RT}\right)}$$

k’ and h are the Boltzmann and Planck’s constants

An Introduction to Mechanisms in Organic Chemistry

The Eyring equation, rearranging gives

$$\ln k = \ln\left(\frac{k'\,T}{h}\right) - \frac{\Delta G^{\ddagger}}{RT} \longrightarrow \ln k = \ln T + \ln\left(\frac{k'}{h}\right) - \frac{\Delta G^{\ddagger}}{RT}$$

$$\longrightarrow \ln\left(\frac{k}{T}\right) = -\frac{\Delta G^{\ddagger}}{RT} + \ln\left(\frac{k'}{h}\right)$$

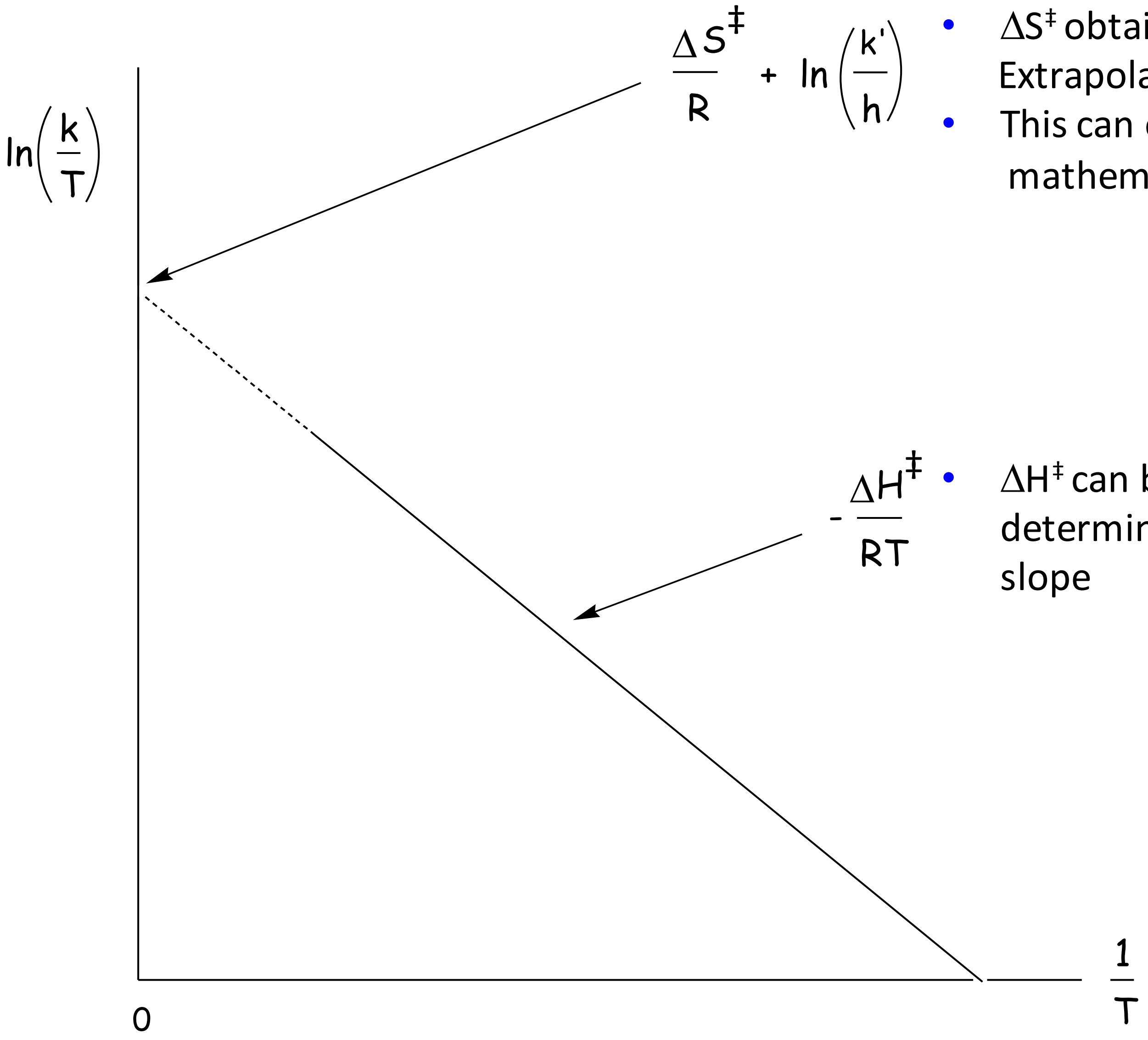
Recall that $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

So

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k'}{h}\right)$$

We can therefore make an Eyring plot of ln (k/T) vs 1/T and should obtain a linear relationship

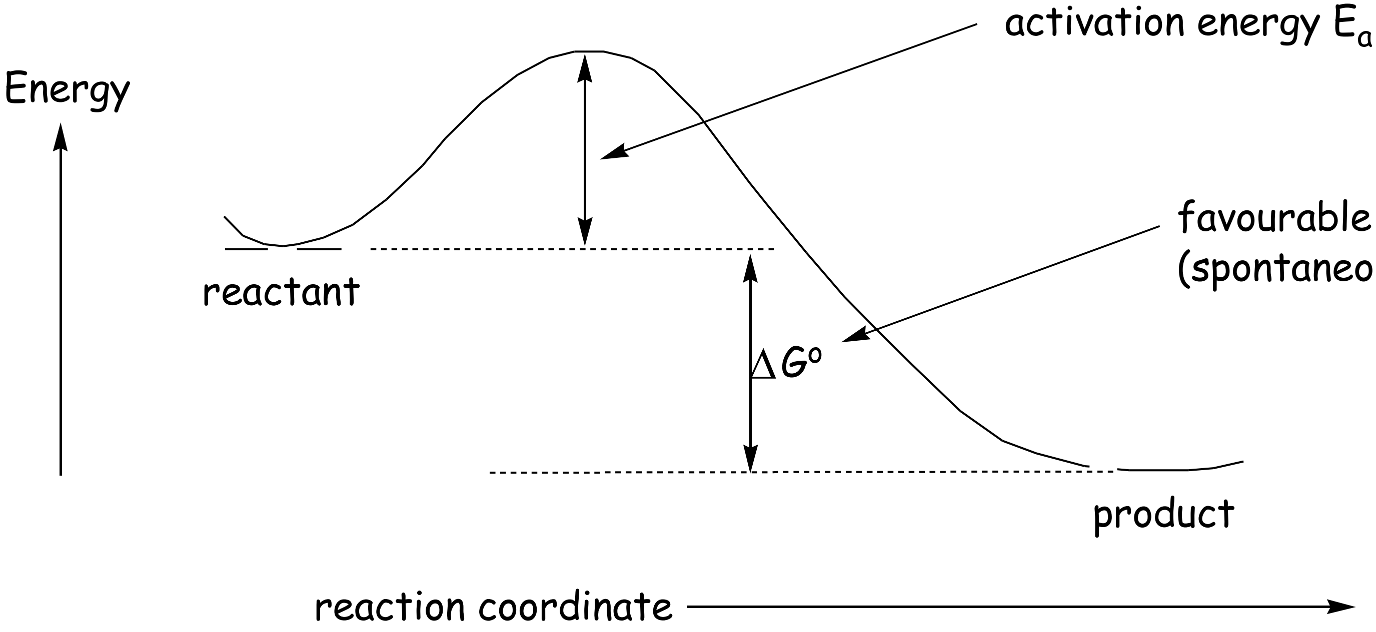
The Eyring Plot



- $\Delta S^\ddagger$ obtained from Extrapolation to infinite T
- This can only determine mathematically

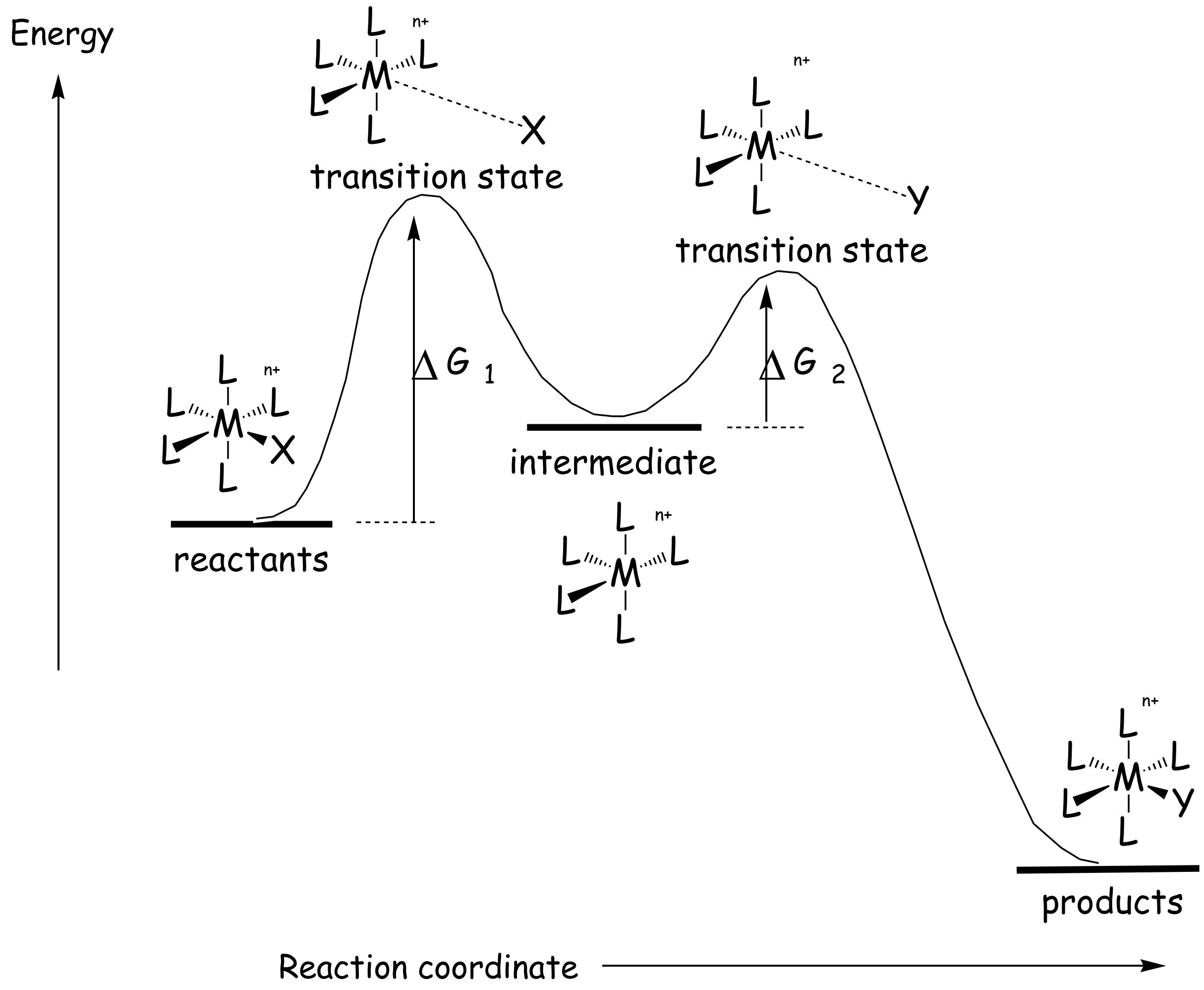
- $\Delta H^\ddagger$ can be accurately determined from the slope

This energy diagram represents a concerted reaction without intermediates



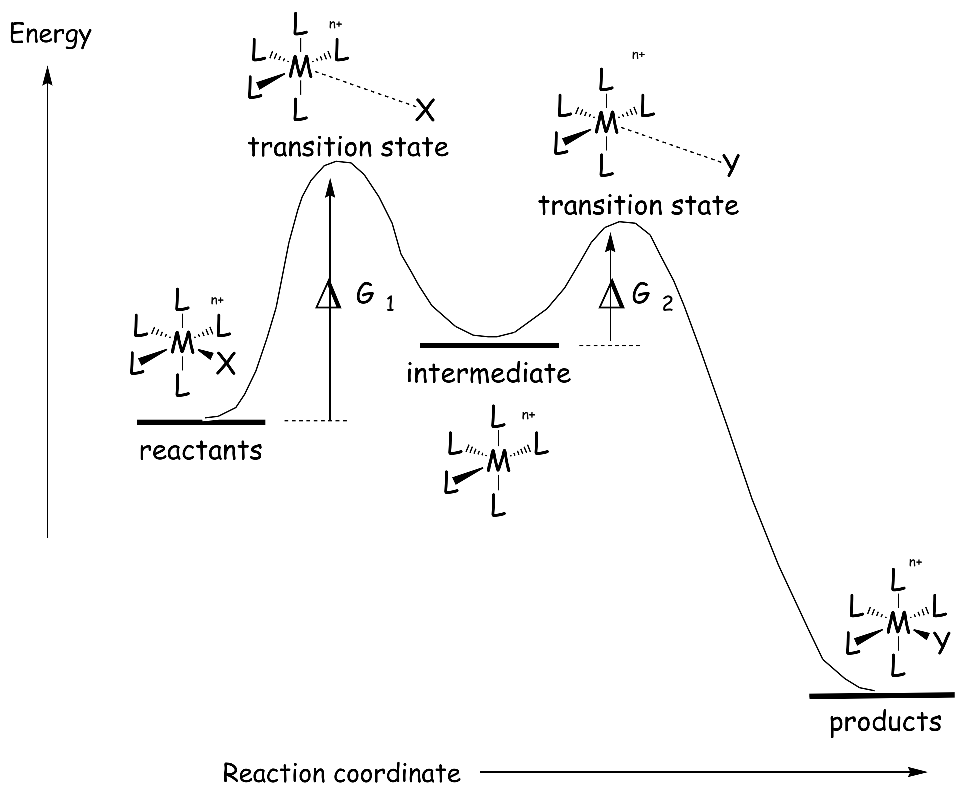
An Introduction to Mechanisms in Organic Chemistry

This energy diagram represents a two-step reaction with an intermediate

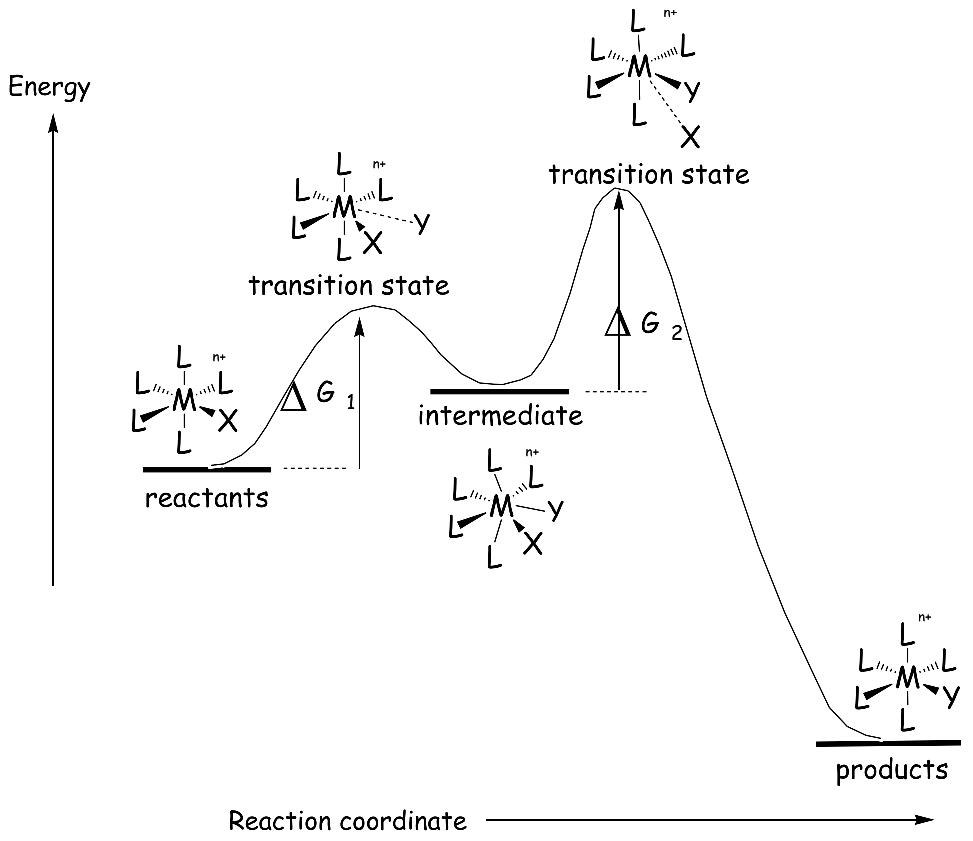


Let’s look at the difference between associative and dissociative processes

A dissociative process



An associative process



Let’s look at some examples
Water exchange on aqua metal ions

	Metal ion	d^n config	Mechanism	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ J K^{-1} mol^{-1}
increasing e_g occupancy ↓	$[V(H_2O)_6]^{2+}$	$t_{2g}{}^3 e_g{}^0$	associative	62	~0
increasing t_{2g} occupancy ↓	$[Mn(H_2O)_6]^{2+}$	$t_{2g}{}^3 e_g{}^2$	associative	33	+6
	$[Fe(H_2O)_6]^{2+}$	$t_{2g}{}^4 e_g{}^2$	increasingly dissociative ↓	41	+21
	$[Co(H_2O)_6]^{2+}$	$t_{2g}{}^5 e_g{}^2$		46	+37
	$[Ni(H_2O)_6]^{2+}$	$t_{2g}{}^6 e_g{}^2$		57	+32

- Increasing e_g occupancy leads to higher lability (smaller $\Delta H^\ddagger$) but doesn’t change the mechanism
- Increasing t_{2g} occupancy correlates with an increase in $\Delta H^\ddagger$ and a more positive $\Delta S^\ddagger$ and leads to dissociative behaviour

Let’s look at some examples

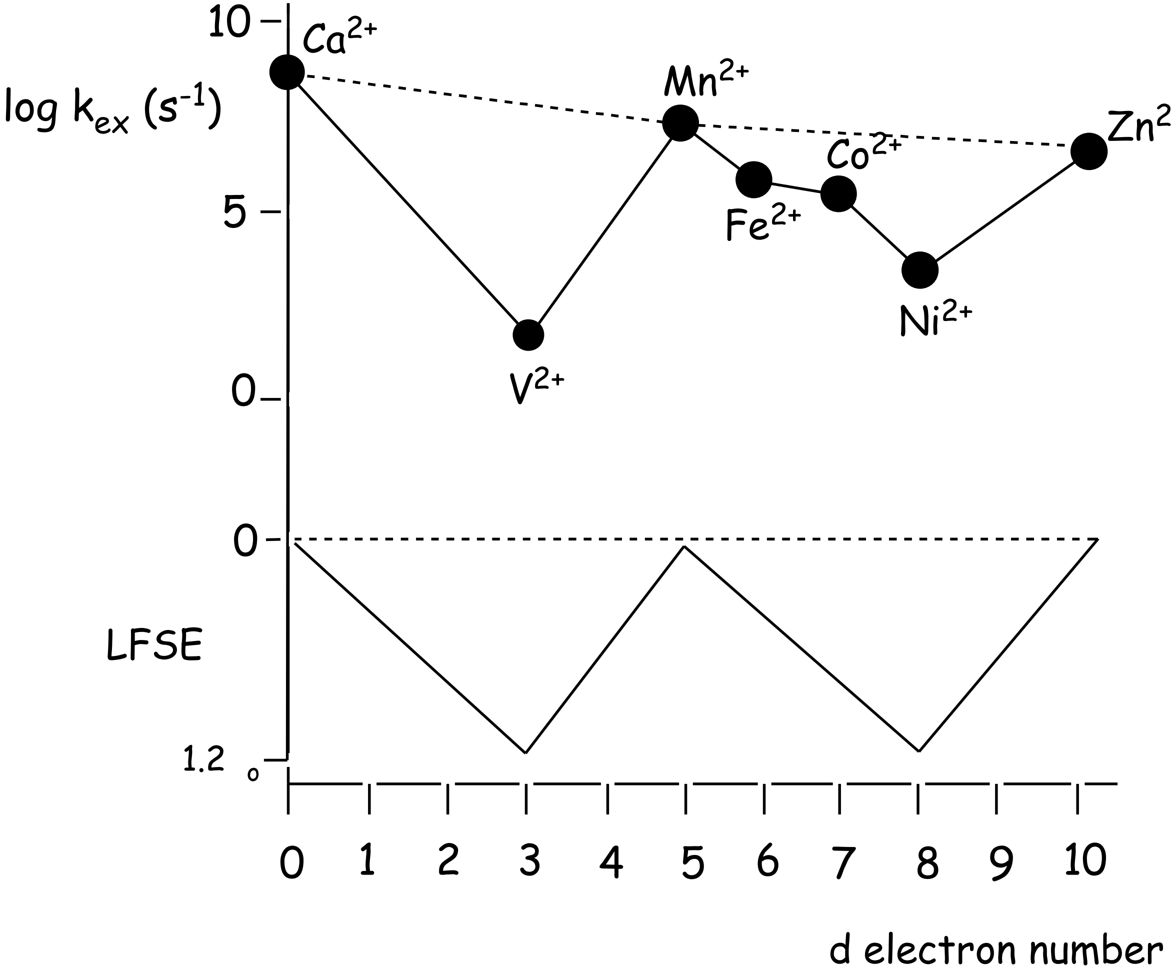
Water exchange on aqua metal ions

	Metal ion	d^n config	Mechanism	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	LFSE units of $_o$
increasing e_g occupancy ↓	$[V(H_2O)_6]^{2+}$	$t_{2g}^3 e_g^0$	associative	62	~0	-1.2
	$[Mn(H_2O)_6]^{2+}$	$t_{2g}^3 e_g^2$	associative	33	+6	0
increasing t_{2g} occupancy ↓	$[Fe(H_2O)_6]^{2+}$	$t_{2g}^4 e_g^2$	increasingly dissociative ↓	41	+21	-0.4
	$[Co(H_2O)_6]^{2+}$	$t_{2g}^5 e_g^2$		46	+37	-0.8
	$[Ni(H_2O)_6]^{2+}$	$t_{2g}^6 e_g^2$		57	+32	-1.2

- $\Delta H^{\ddagger}$ correlates with LFSE, which is a measure of the strength of the M-OH_2 bond
- However, $\Delta H^{\ddagger}$ is of limited use as a mechanistic indicator

An Introduction to Mechanisms in Organic Chemistry

We saw previously that k_{ex} correlates with LFSE
We can now deduce that k_{ex} correlates with $\Delta H^{\ddagger}$
This is entirely expected as, regardless of mechanism, there will be a bond-breaking event along the reaction coordinate (most endothermic step of the reaction, most impacting the rate)



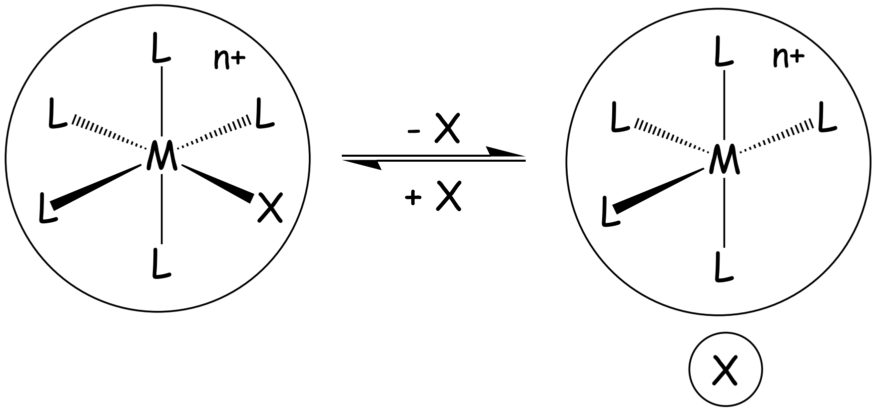
Let’s look at some examples
Water exchange on aqua metal ions

	Metal ion	d^n config	Mechanism	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}	LFSE units of $_o$
increasing e_g occupancy ↓	$[V(H_2O)_6]^{2+}$	$t_{2g}^3\ e_g^0$	associative	62	~0	-1.2
	$[Mn(H_2O)_6]^{2+}$	$t_{2g}^3\ e_g^2$	associative	33	+6	0
increasing t_{2g} occupancy ↓	$[Fe(H_2O)_6]^{2+}$	$t_{2g}^4\ e_g^2$	increasingly dissociative ↓	41	+21	-0.4
	$[Co(H_2O)_6]^{2+}$	$t_{2g}^5\ e_g^2$		46	+37	-0.8
	$[Ni(H_2O)_6]^{2+}$	$t_{2g}^6\ e_g^2$		57	+32	-1.2

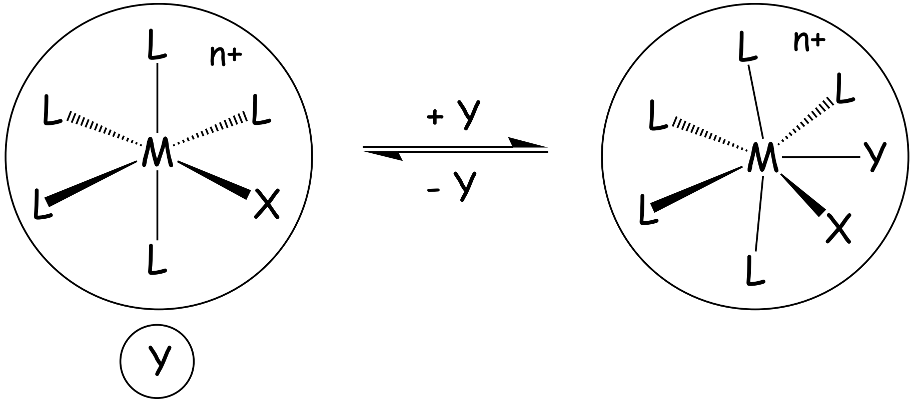
- $\Delta S^‡$ to a certain extent correlates with with the mechanistic trend BUT this value is prone to large errors based on the mathematical extrapolation to infinite T
- Is there another parameter available that we can use as an indicator of the mechanistic pathway? **YES**

The activation volume: $\Delta V^{\ddagger}$
Consider the two pathways again:

DISSOCIATIVE



ASSOCIATIVE



- The dissociative process with have a positive $\Delta V^{\ddagger}$
- The increase in $\Delta V^{\ddagger}$ corresponds to the volume of free X

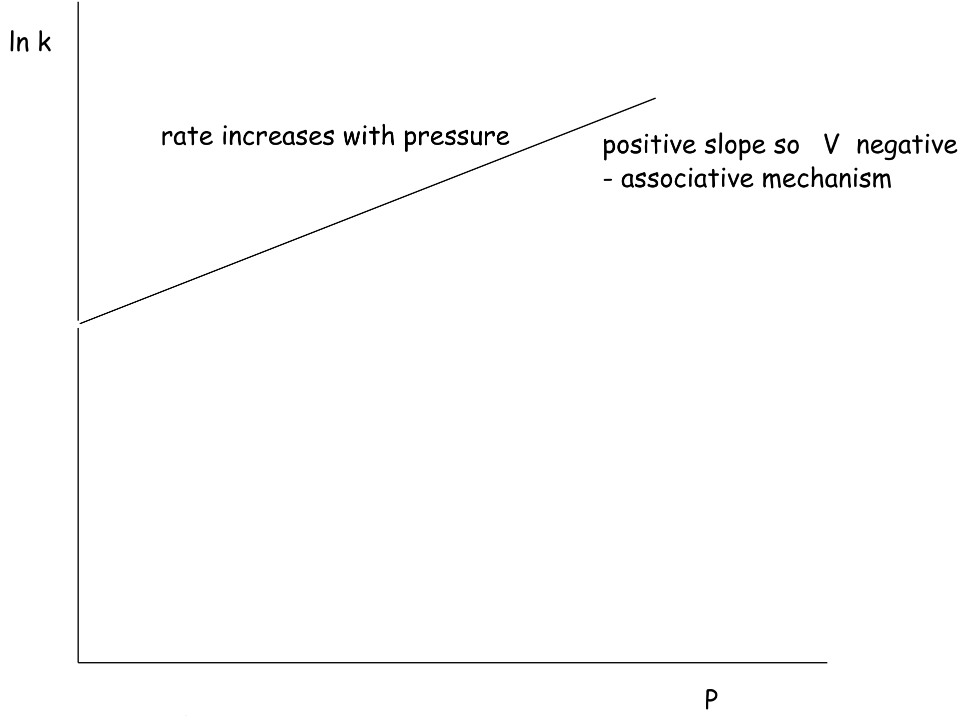
- The associative process with have a negative $\Delta V^{\ddagger}$
- The decrease in $\Delta V^{\ddagger}$ corresponds to the volume of free Y

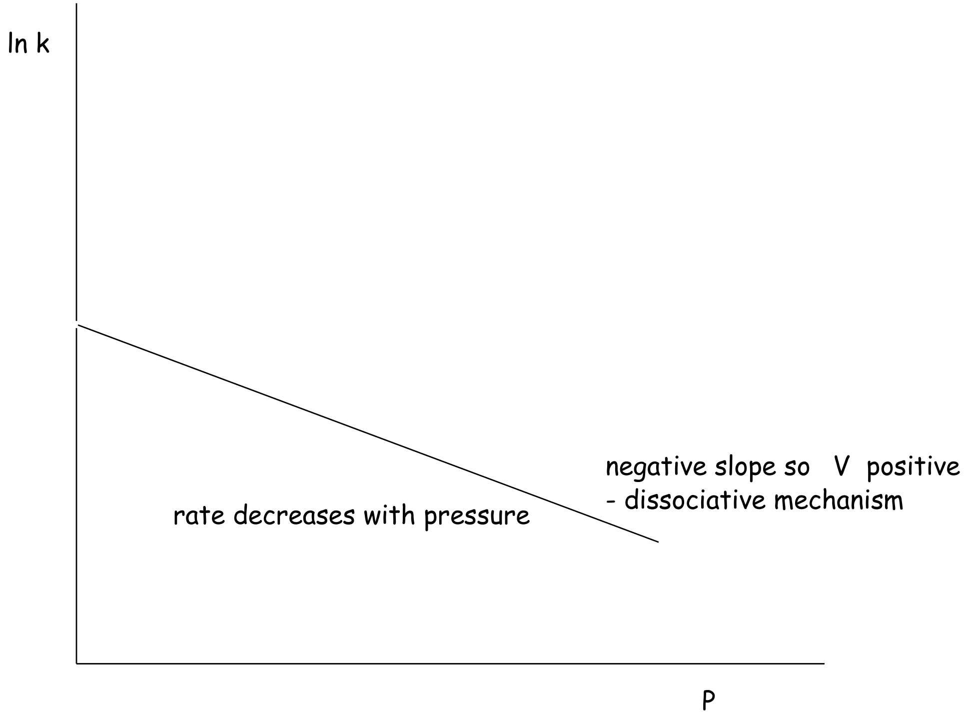
How do we measure $\Delta V^{\ddagger}$?

From the pressure dependence of the reaction rate:

$$\frac{d(\ln k)}{dP} = \frac{-\Delta V^{\ddagger}}{RT}$$

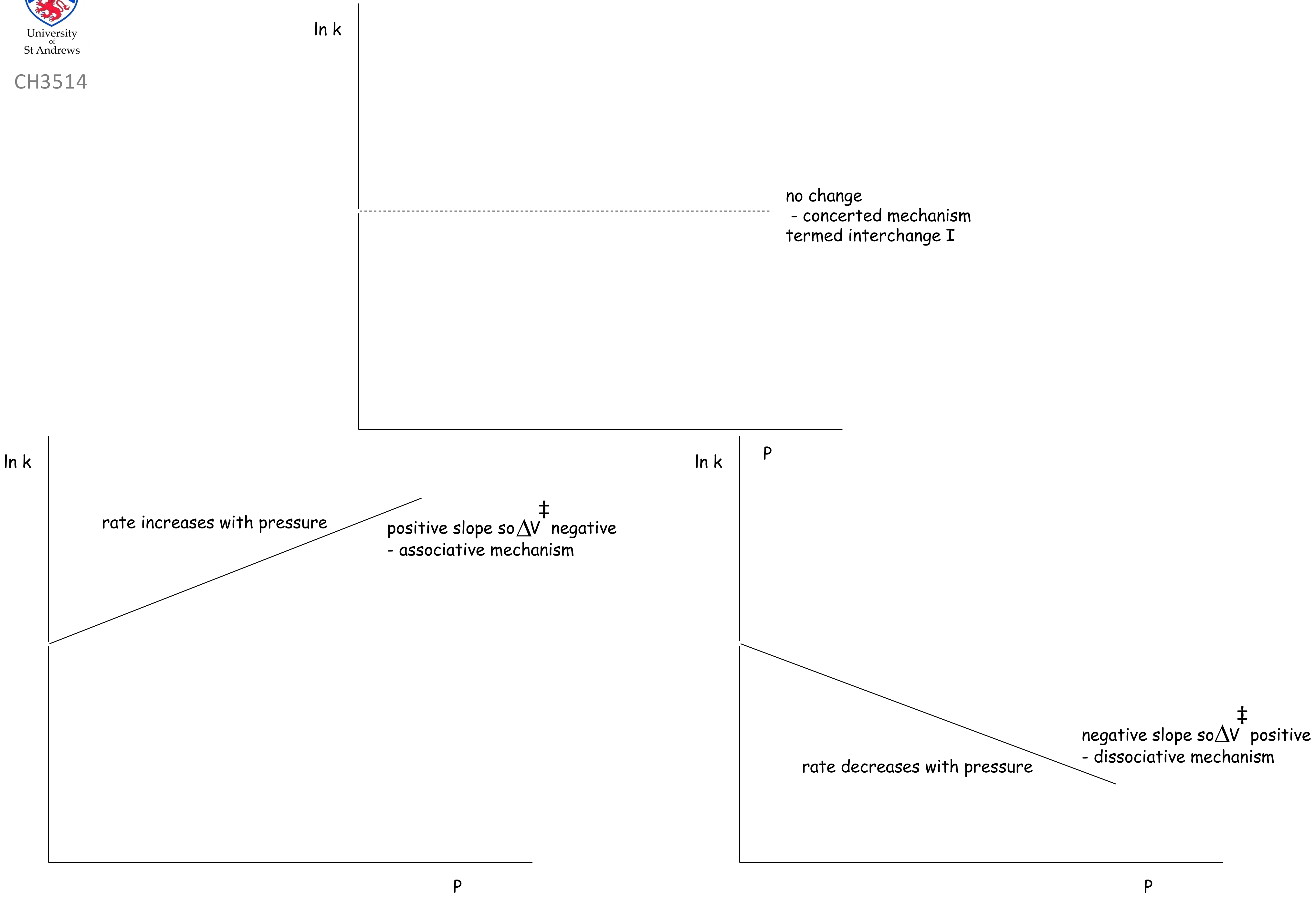
A plot of ln k vs P will provide a slope of $-\Delta V^{\ddagger}/RT$





Housecroft and Sharpe, page 883

An Introduction to Mechanisms in Organic Chemistry



no change
- concerted mechanism
termed interchange I

rate increases with pressure

positive slope so $\Delta V^{\ddagger}$ negative
- associative mechanism

rate decreases with pressure

negative slope so $\Delta V^{\ddagger}$ positive
- dissociative mechanism

Housecroft and Sharpe, page 883

An Introduction to Mechanisms in Organic Chemistry

We can now appreciate why various mechanisms would have such rate/pressure dependencies

A **dissociative** process involves the expulsion of the leaving ligand X (expansive) so would be expected to be retarded by applying pressure

negative slope - positive activation volume

An **associative** process involves the take up of Y (compressive) so would be expected to be accelerated by applying pressure

positive slope - negative activation volume

Let's go back to the previous example:

	Metal ion	d^n config	Mechanism	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ J K^{-1} mol^{-1}	$\Delta V^\ddagger$ cm^3 mol^{-1}
increasing e_g occupancy ↓	$[V(H_2O)_6]^{2+}$	$t_{2g}^3 e_g^0$	associative	62	~0	-4.1
increasing t_{2g} occupancy ↓	$[Mn(H_2O)_6]^{2+}$	$t_{2g}^3 e_g^2$	associative	33	+6	-5.4
	$[Fe(H_2O)_6]^{2+}$	$t_{2g}^4 e_g^2$	increasingly dissociative ↓	41	+21	+3.7
	$[Co(H_2O)_6]^{2+}$	$t_{2g}^5 e_g^2$		46	+37	+6.1
	$[Ni(H_2O)_6]^{2+}$	$t_{2g}^6 e_g^2$		57	+32	+7.2

- $\Delta V^\ddagger$ is a good indicator of mechanism

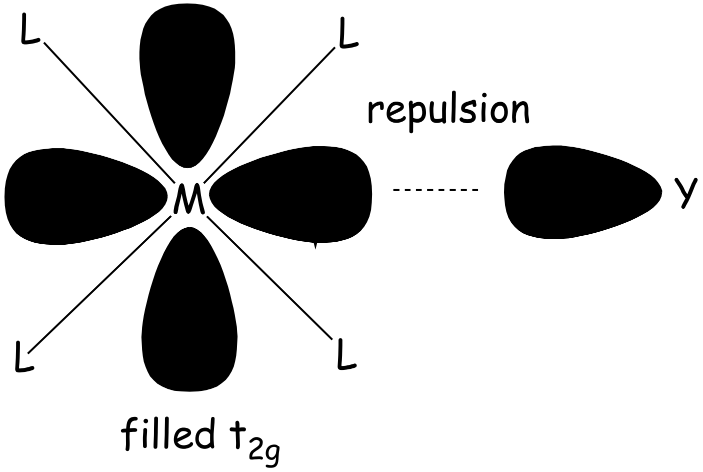
- Increase in e_g occupancy **lowers** $\Delta H^\ddagger$ but doesn't change the mechanism
  – still **associative**
- Increase in t_{2g} occupancy **increases** $\Delta H^\ddagger$ AND gives positive values for $\Delta V^\ddagger$
  – more **dissociative**

An Introduction to Mechanisms in Organic Chemistry

We can understand these trends from an MO perspective

Increasing e_g occupancy weakens (lengthens) the resident M-OH_2 bonds – lowers LFSE and $\Delta H^{\ddagger}$ and increases the rate of exchange

However, increasing t_{2g} occupancy will repel the electrons on the entering ligand Y - facilitating the **dissociative** pathway



University of St Andrews

CH3514

Summary

- ✓ LFT and in particular σ-donor, π-donor and π-acceptors and how they influence Δ_o
- ✓ Hydrolysis chemistry of metal complexes
- ✓ Thermodynamics of metal complex formation (K, β, ΔG_o)
- ✓ HSAB chemistry
- ✓ The origins of the Irving-Williams Series and the JT effect
- ✓ The chelate effect
- ✓ The factors governing the stabilities of oxidation states
- ✓ Quantification of oxidizing and reducing strength by electrochemistry (E^o_{cell}, ΔG^o_{cell})
- ✓ Delineation between thermodynamic stability and kinetic inertness