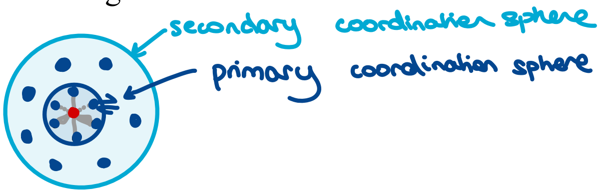
WEEK 1

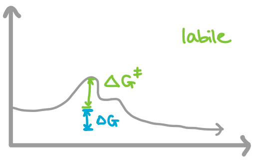
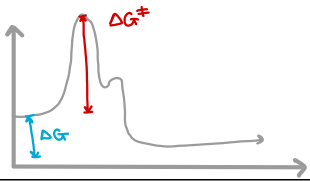
Water exchange in octahedral complexes:

k (rate constant) measures the rate of exchange between the first and second coordination spheres.



Small $\Delta G^{\ddagger}$	**Large $\Delta G^{\ddagger}$**
Fast reaction Metal complex is labile $t_{\frac{1}{2}} < 1\text{min}$	Slow reaction Metal complex is intert $t_{\frac{1}{2}} > 1$ min

Exchange rates for water ligands vary depending on the metal centre.

Large *k*	Small *k*
Low charge density	Large charge density
Ion size is large	Ion size is small
Small charge to size ratio	Large charge to size ratio
Fast rate of exchange	Slow rate of exchange
	

LFSE Effects in water exchange: stabilised

slow exchange rate

d^0 d^6 d^3 d^4 d^5 d^8 d^6 stabilised (LFSE)

$V^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < Zn^{2+} < Cr^{2+} < Cu^{2+}$ fastest exchange rate (destabilised)

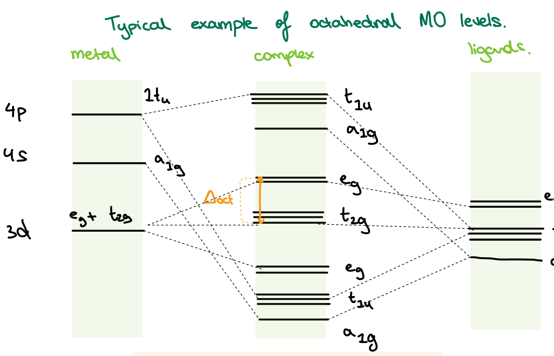
no LFSE (CFSE e^- diagrams)

Loss of Ligand Field Stabilisation ⇒ increase in E_a ⇒ decrease in rate of ligand exchange

Recap of LFSE

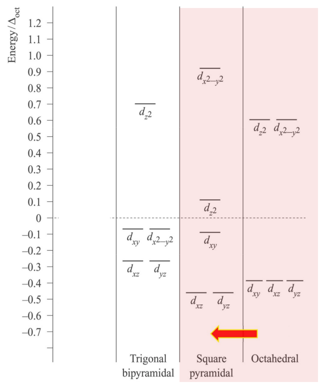
→ application of MO theory which describes the origins of Δ_{oct}.
1. metal ligand σ bonding
2. effects of π bonding
3. complexes with similar symmetry

Typical example of octahedral MO levels.

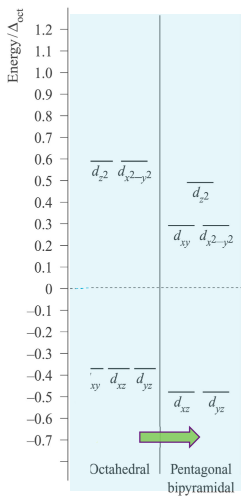


A good σ-donor ligand results in strong metal-ligand overlap
⇒ more strongly antibonding e_g set.
≡ Larger Δ_{oct}.

For I_d mechanisms;
coordination numbers: 6 → 5



For I_a mechanisms;
coord: 6 → 7.



Mechanisms for Ligand Substitution & Activation Parameters

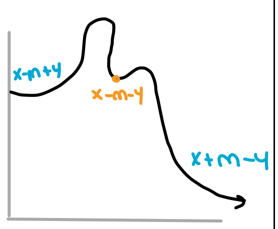
reaction rate is independent to conc. and nature of incoming ligand.

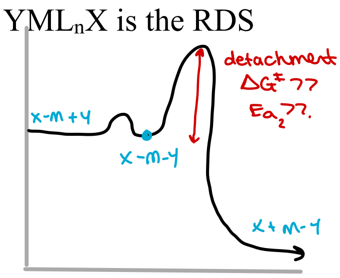
Mechanisms with detectable intermediates:

Associative

Favoured for:
- ★ metals with low e⁻ density
- ★ bad leaving groups (strong base strong e⁻ donating ligand)

a activated	d activated
Attachment of Y to ML_nX is the RDS	Detactment of X from YML_nX is the RDS

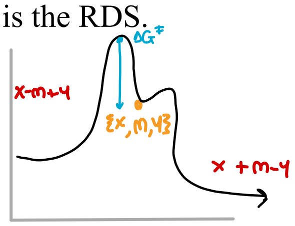


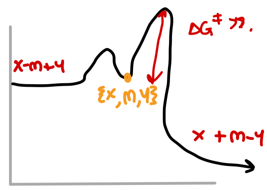


Dissociative

Favoured for:
- ★ high e⁻ density metals
- ★ good leaving group ligands ⇒ weak bases, e⁻ poor ligands.

a activated	d activated
Attachment of X to ML_n in {X, ML_nX, Y} is the RDS.	Detatchment of ML_nX is the RDS.





Mechanisms without a detectable intermediate – Interchange Mechanism
Transition state cannot be detected or isolated, but can be calculated
There is no well-defined energy minimum
Most substitution reactions follow this mechanism

RATE DETERMINING STEPS

Interchange Associative (I_a)
Rate depends on strongly on nature of entering group

Interchange Dissociative (I_d)
1. Little/no rate dependence on nature of entering group 2. Strong rate dependence on nature of leaving group 3. Increase in charge causes decrease in rate