Name: _____   Date: _____

2021 SMTP-GATE C2 Chemistry
Transition Elements – Crystal Field Theory

Resources:
A Guided Inquiry Activity for Teaching Ligand Field Theory, Brian J. Johnson and Kate J. Graham

Part 1 – Crystal Field Theory for an octahedral complex

Crystal field theory is a model based on the repulsion of metal d electrons by the electrons of the ligands.

Ligands *are ions or neutral molecules that bond to a central metal atom or ion, resulting in a* ***complex*** *being formed.*

Q1   In the space below, draw all the d orbitals of a transition metal ion.

d_{xy} d_{xz} d_{yz}

$d_{x^2-y^2}$ d_{z^2}
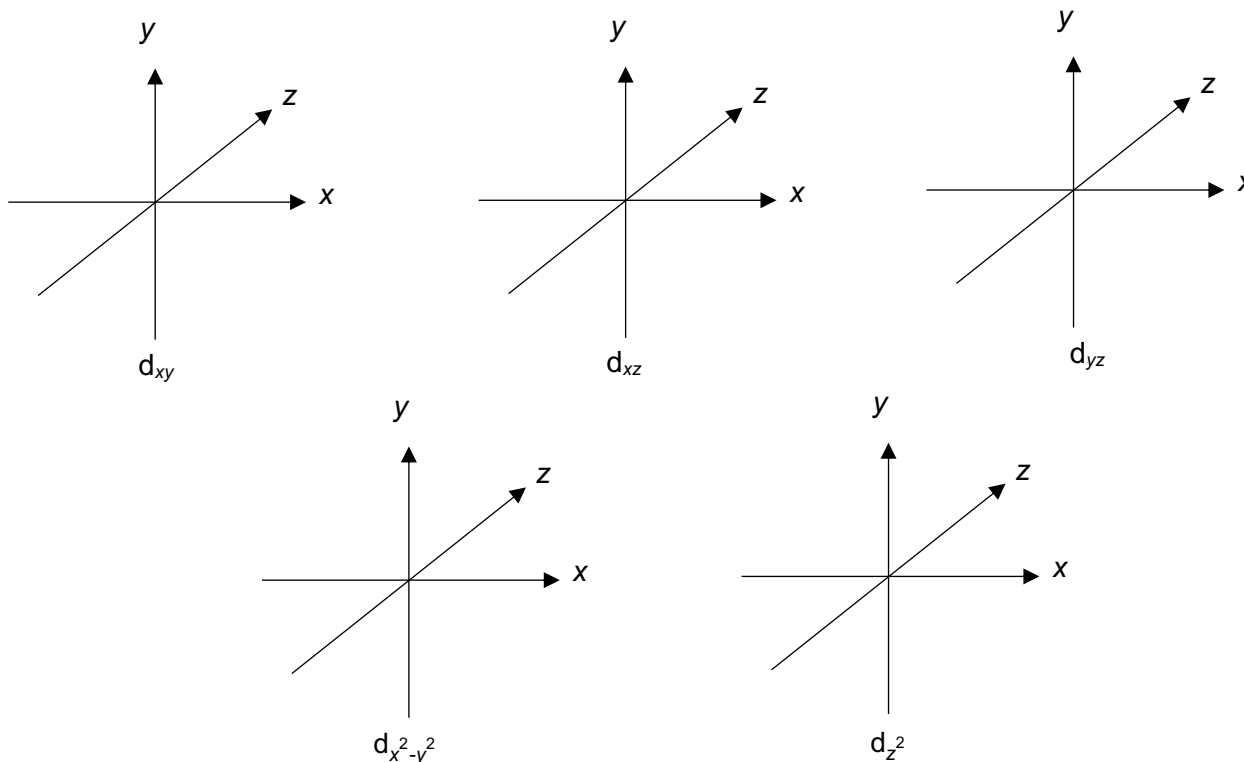
Consider a ligand (which can be taken as a ***negative point charge***) approaching the transition metal ion.

- With no ligand present, the five d orbitals are equivalent in energy (degenerate).

- In a presence of ligands (in a uniform, spherical field of negative charge), the orbitals go to a higher energy (while remaining degenerated) due to electron-electron repulsion (see Page 2).

- When the **6** ligands are placed in **an octahedral arrangement** (with respect to the transition metal ion) on the *x*, *y* and *z*-axes, there will be a splitting of the *d*-orbitals to different energy levels.
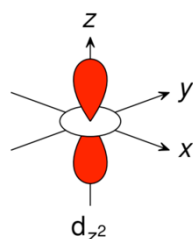
Q2   On the diagram below, position the 6 ligands appropriately given the position of the metal ion. These 6 ligands have an octahedral geometry with respect to the metal ion.

| Represent the ligand as L. |
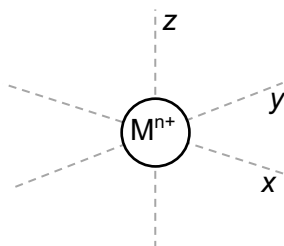
Consider a ligand approaching the metal ion from the **z**-axis.

The d_{z^2} orbital is given below.

d_{z^2}

Q3   Briefly explain why the potential energy of the orbital will increase.

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Q4   A ligand can also approach the *x* and *y*-axes with the same probability as that of the *z*-axis. From your drawings in **Q1**, which other orbital will experience an increase in potential energy, for the same reason cited in **Q3**? (There's only 1 other orbital!)

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The 2 orbitals identified in **Q3** and **Q4** will experience an increase in potential energy. They are also known as the e_g orbitals. Due to the conservation of energy, the 3 other orbitals will hence experience a decrease in potential energy. These 3 orbitals are the t_{2g} orbitals. The figure below illustrates this concept.
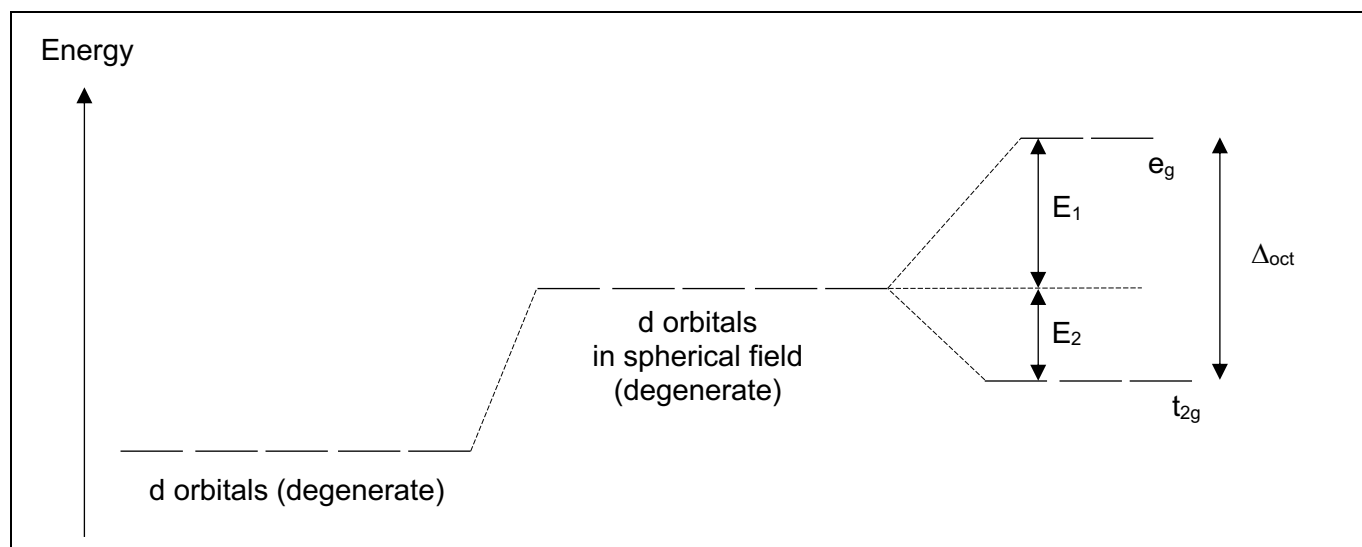
Remember to refer to this diagram in subsequent parts to help in your visualisation.

Refer to the diagram on the previous page.

E_1 is the *increase* in energy of <u>1</u> degenerate d orbital to become an e_g orbital, and E_2 is the *decrease* in energy of <u>1</u> degenerate d orbital to become a t_{2g} orbital.

Q5(a)   State how E_1, E_2 and Δ_{oct} are related to each other: ……………………………………………

Q5(b)   Express the total increase in energy of both e_g orbitals in terms of E_1, and the total decrease in energy in terms of E_2.
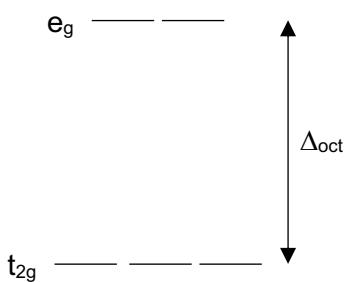
Q5(c)   Keeping in mind that the total increase in energy of both e_g orbitals is the same as the total decrease in energy of all t_{2g} orbitals, construct another equation relating E_1 and E_2.

Q5(d)   Hence, using the 2 equations from (a) and (c), show that $E_1 = 0.6\ \Delta_{oct}$, and $E_2 = 0.4\ \Delta_{oct}$.

The splitting of the d-orbitals into two groups by ligands is known as ligand field splitting. This energy gap, Δ_{oct}, is dependent on the exact identities of the metal and the ligands.

The terms *weak field* and *strong field* give an indication of the extent of the splitting of the d-orbitals by the ligands.

Strong field	Weak field
e_g — — Δ_{oct} t_{2g} — — — In a strong field, the splitting parameter, Δ_{oct}, is large.	e_g — — Δ_{oct} t_{2g} — — — In a weak field, the splitting parameter, Δ_{oct}, is small.
High / low spin (circle one)	High / low spin (circle one)

Q6 Imagine promoting a single electron from a lower energy d-orbital to a higher energy d-orbital. Would it be easier to promote it in a <u>strong field</u> or <u>weak field</u>? (Circle your answer)

Q7 Write the electronic configuration for Co^{2+} in $[Co(H_2O)_6]^{2+}$. (Atomic number of Co is 27.) We say that this is a <u>d^n octahedral complex</u> as the 6 H_2O ligands are orientated in an octahedral configuration about the Co^{2+} ion. State the value of n in this case.

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How the electrons fill up the d-orbitals will differ for strong field and weak field complexes.

• When Δ_{oct} is large, the lower energy d-orbitals are filled first by pairing up if necessary, before the higher energy d-orbitals are used. This is known as 'low spin' state.

• When Δ_{oct} is small, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals. This is known as 'high spin' state.

Q8 *If* $[Co(H_2O)_6]^{2+}$ is a strong field complex, using the diagram above, show how the d electrons in Co^{2+} will be distributed. Do the same *if* $[Co(H_2O)_6]^{2+}$ is a weak field complex instead.

Q9 Complexes with a strong field are often called **low / high spin** (circle one).

Complexes with a weak field are often called **low / high spin** (circle one).

Complete the second row in the table above.

We will now attempt to explain the allocation of electrons in their respective orbitals for a strong and weak field using **Model 1**.

Model 1 - The ligand field energy, E

Please refer to the diagram on page 2 when interpreting the formula.

We can calculate the ligand field energy using the following formula:

Ligand field energy, E =
- (number of electrons in t_{2g} orbitals) × E_2
+ (number of electrons in e_g orbitals) × E_1
+ (number of electron pairs) × P

Whether a high or low spin is favoured depends on E. **The spin that results in a lower E is favoured.**

By default, an electron will always fill up a t_{2g} orbital <u>singly</u> first (like how you fill any subshell singly before pairing electrons up). If it cannot, it can either

1   pair up with one electron in a t_{2g} orbital (for low spin); <u>OR</u>
2   fill up an e_g orbital (for high spin)

if electron has the luxury of choice.

1   Pairing up with one electron in an t_{2g} orbital results in an increase in potential energy of a system due to inter-electronic repulsion of the paired electrons. This increase in potential energy is known as the pairing energy, P.
2   Filling up 1 electron in an e_g orbital will result in an increase in potential energy of a system by the splitting parameter, $\Delta_{oct} = E_1 + E_2$.

For example, for a d^4 octahedral complex:
If the complex has a **high** spin (weak field), 3 electrons are in the t_{2g} orbitals, while 1 electron is in the e_g orbitals. None of the electrons are paired up.

- $E_{\textbf{high spin}} = -3E_2 + E_1 + 0P$ t_{2g} [↑ | ↑ | ↑] e_g [↑ |]

If the complex has a **low** spin (strong field), all 4 electrons are in the t_{2g} orbitals (no electrons in the e_g orbitals). Note that 2 electrons in the t_{2g} orbitals are paired with each other in 1 t_{2g} orbital (so there is only 1 electron pair).

- $E_{\textbf{low spin}} = -4E_2 + 0E_1 + 1P$ t_{2g} [↑↓ | ↑ | ↑]

Q10   Calculate the ligand field energy for $[Co(H_2O)_6]^{2+}$ if $[Co(H_2O)_6]^{2+}$ is a strong field complex and weak field complex respectively. Express your answer in terms of Δ_{oct} and P.

Strong Field (Low Spin)	Weak Field (High Spin)

Q11   If $E_{high\ spin} < E_{low\ spin}$, then a high / low spin will be adopted. (circle one)

If $E_{low\ spin} < E_{high\ spin}$, then a high / low spin will be adopted. (circle one)

Hence, deduce an inequality concerning P and Δ_{oct} given that $[Co(H_2O)_6]^{2+}$ is a weak field complex.
After simplifying the inequality, what can you conclude about P and Δ_{oct} for a weak field complex?
What if $[Co(H_2O)_6]^{2+}$ is a strong field complex?

Part 3a – Effect of Metal Ion and Ligands

Given that $E = \dfrac{hc}{\lambda}$, the separation between the energy levels can be given in three different ways:

- In units of cm^{-1} (Wavenumber $= \dfrac{1}{\lambda}$)
- In energy units
- In units of wavelength

The Δ_{oct} values for different complexes are shown below.

Given that electrons are more likely to pair up if Δ_{oct} values are bigger than 17000 cm^{-1} (P = 17000 cm^{-1}), complete the table below.

Complex ion	Δ_{oct} / cm^{-1}	High spin or low spin
$[Cr(H_2O)_6]^{2+}$	9250	
$[Cr(H_2O)_6]^{3+}$	17400	
$[Co(H_2O)_6]^{2+}$	10200	
$[Co(H_2O)_6]^{3+}$	22900	
$[Rh(H_2O)_6]^{3+}$	33400	
$[Ir(H_2O)_6]^{3+}$	41000	

Q12 Using the data in the table above, state how Δ_{oct} varies with charge of the metal ion and suggest a reason for the variation.

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Q13 Using the data in the table above, state how Δ_{oct} varies with metal complexes down the group and suggest a reason for the variation.

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Part 3b – Effect of Ligands

Below are some data for octahedral Ti^{3+} complexes. Rank the ligands in increasing order in terms of their ability to split the d-orbitals (1 being the smallest; 4 being the largest).

Ligand	Wavenumber / cm^{-1}	Ranking
H_2O	19000	
F^-	17000	
Cl^-	11800	
Br^-	10500	

Below are some data for octahedral Cr^{3+} complexes. Rank these ligands in increasing order in terms of their ability to split the d-orbitals (1 being the smallest; 5 being the largest).

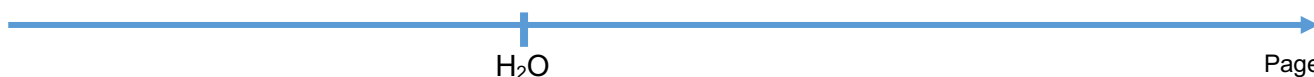| Ligand	λ / nm	Ranking
H_2O	575	
SCN^-	562	
NH_3	465	
en, ethylenediamine	463	
CN^-	374	

Below are some data for octahedral Co^{3+} complexes. Rank these ligands in increasing order in terms of their ability to split the d-orbitals (1 being the smallest; 5 being the largest).

Ligand	Δ_{oct} / kJ mol^{-1}	Ranking
F^-	156	
NH_3	273	
en, ethylenediamine	285	
H_2O	217	
CN^-	400	

Q14 On the axis below, combining the information from the tables on the same page, produce a consistent ranking of the ligands in terms of their ability to split d orbitals.

Small splitting (lower Δ_{oct})   Large splitting (higher Δ_{oct})

H_2O

The magnitude of Δ_{oct} can most easily be measured using UV-visible spectroscopy.

Q15 Consider a d^1 complex with energy gap Δ_{oct}. When it absorbs light with energy corresponding to Δ_{oct}, the electron is promoted from the lower energy t_{2g} orbitals to the higher energy e_g level orbitals. This is called a **d-d transition**.

Redraw the five orbitals to show the new electron arrangement.

_____ _____   _____ _____

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_____ _____ _____   _____ _____ _____

Ground state   Excited state
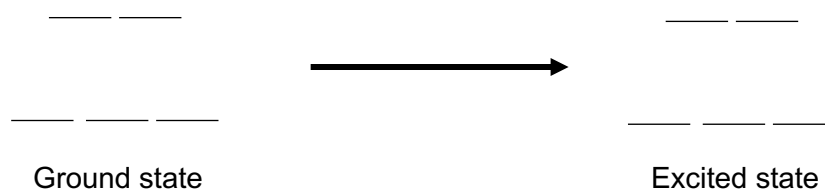
As Δ_{oct} varies, the colour of the compound will change.
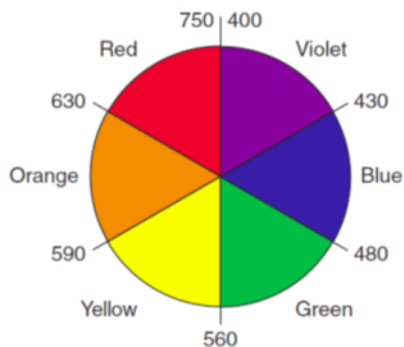
Q16 Consider an octahedral metal complex that absorbs light at 510 nm. It appears to be red in colour when observed.

Is the wavelength of the light absorbed the same as that observed? If not, what is their relationship?

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Summary

- For transition metal complexes to appear coloured, the d-orbitals must be partially filled.
- In the presence of ligands, the degenerate 3d orbitals of a transition metal ion are split into 2 different energy levels.
- There is a small energy gap Δ_{oct} between the 2 energy levels with vacancies in the **higher / lower** energy d orbitals. (circle one)
- The **absorption / transmission** (circle one) of radiation in the visible spectrum with energy corresponding to the energy gap will cause an electron to be promoted from the lower to the higher energy level.
- The colour observed is the complement of the colours absorbed.

Practice Problems

1   If a solution appears yellow, what wavelength of light does it absorb?

2 $[Ti(H_2O)_6]^{2+}$ absorbs light around 500 nm. What colour will it appear as?

3   You have two solutions, one which is orange in colour, and another that is blue in colour. You know that both solutions are made up of a cobalt complex. However, only one has chloride ions as ligands, while the other has ammonia ligands. Which solution would you expect to be the one that is orange in colour?

4 $[Cu(H_2O)_6]^+$ is completely colourless while $[Cu(H_2O)_6]^{2+}$ is blue. Draw the d orbitals splitting diagrams to explain this observation.