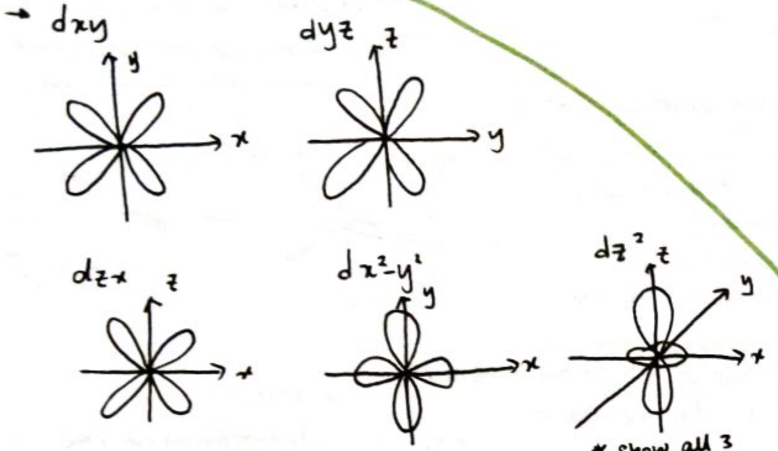
TRANSITION METALS

D-ORBITALS



* show all 3 axis

- → all are degenerate (same E level)

METALLIC PROPERTIES

- → giant metallic lattices
- → Strong metallic bonds ∵ Small size & close packing of atoms (+5 +6 etc)
- → ∴ ↑mp ↑bp than s-block.

MEASURING CONC.

- → visible spectroscopy
- → colorimetry.

VARIABLE OXIDATION STATE

- → arises from similar energies required for removing 4s and 3d e⁻
- → all have +2 oxi state except Sc.
- → +4 → +7 bonded to O
  - ↳ High IE compensated by energy given out via bond formation between metal & O
- → only Cu have +1

COLOURED IONS

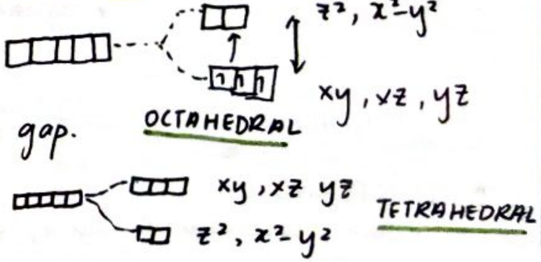
- → Ions with d^{10} / d^0 → colourless.
- → Colour caused by ease of transition of e⁻ between E-levels.
- → colour depends on : transition element, oxi state, ligand, coordination number.

TRANSITION ELEMENTS

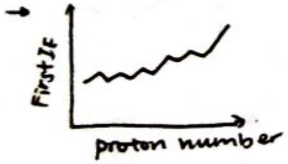
- ⇒ An element that forms at least one ion with an incomplete d sub-shell
- → * Sc^{3+} - $[Ar]3d^0$, Zn^{2+} $[Ar]3d^{10}$ → not transition metals.
- → Cr - $[Ar]\ 3d^5 4s^1$ → ½ filled ∴ equal distribution of charge
  Cu - $[Ar]\ 3d^{10}4s^1$ → filled 3d & ½ filled 4s = more stable.
- → All transition elements loses e⁻ from 4s ∴ all have similar chemical properties.

SPLITTING OF D ORBITALS

- → Usually 3d orbitals all have same energy.
- → Repulsion between e⁻ in ligand and 3d e⁻ of metal ↑ energy of 3d orbitals of transition metals in the complex.
- → e⁻ occupy lower orbitals BUT can be promoted to higher energy level by absorbing visible light equal to energy gap.



IONISATION ENERGIES



- → little change in 1st IE shows little change in atomic radii & ionic radii
- → ↓ in atomic radii less noticeable. ∴ shows 3d & 4s subshell have similar energy.

COMPLEX IONS

↳ when ligands form dative covalent bonds to a central species such as a transition metal ion.

LIGANDS

↳ atoms / ions which have lpe⁻, form dative covalent bonds to central ion, donate lone pair of e⁻ into vacant orbitals on central species.

- → classified by no. of lp USED.
- → monodentate - ligands which form 2 co-ordinate bonds to a metal ion.
- → bidentate - 2
- → multidentate - several

TRANSITION METALS

NAMING COMPLEXES

- → $[Cu(H_2O)_6]^{2+}$ → if overall -ve ∴ ate
  - hexaaquacopper (II)
  - hexa → no of ligands
  - aqua → ligand name
  - copper → central ion
  - (II) → oxi state.
- → if overall is anionic complex,
  - $[CuCl_4]^{2-}$ tetrachlorocuperate (II)
- * $[MnO_4]^-$ manganate (VII) - SPECIAL CASE -
- → aluminium → aluminate , chromium → chromate
  cobalt → cobalterate , copper → cuperate , iron → ferrate
  silver → argentate , manganese → manganate.

COORDINATION NUMBER

↳ number of dative covalent bonds formed to central metal ion from surrounding ligands

- → change of ligand = change in coodination number (may)
- → co-ordination No → 6 → octahedral
  - 4 → tetrahedral
  - → square planar $[NiCl_4]^{2-}$
  - 2 → linear.

ISOMERISM

→ STRUCTURAL

↳ same molecular formula, diff structural formula.

- → Cl^- { ion → paired w/ complex ion
  - ligand → inside complex ion
- → H_2O { ligand
  - water of crystallisation
- → Eg $CrCl_3(H_2O)_6$

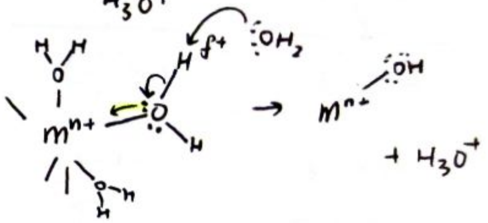
🟪 $[Cr(\overset{L}{H_2O})_6]^{3+}.3\overset{I}{Cl^-}$ → ppt↑ due to ↑ free Cl^- ions.

🟩 pale $[Cr(\overset{L}{H_2O})_5\overset{L}{Cl}]^{2+}.2\overset{I}{Cl^-}.\overset{wc}{H_2O}$

🟩 $[Cr(\overset{L}{H_2O})_4\overset{L}{Cl_2}]^+.\overset{I}{Cl^-}.2\overset{wc}{H_2O}$ → ppt↓

HYDROLYSIS

- → When salts dissolve in H_2O, ions are stabilised by polar water molecules
- → Hydrolysis can occur and resulting solution = acidic
  - → aq metal ions attract H_2O molecules (6)
  - → known as hexaaqua ions (octahedral)
  - → water = Lewis base (lp donor)
  - → ion = Lewis acid (lp acceptor)
  - → water forms dative covalent bond w/ ion.
  - → charge density ↑ , cation = greater attraction
  - → attraction extends to shared pair of e^- in OH bond of H_2O
  - → e^- pair pulled towards O , bond more polar
- → H more acidic (more δ+)
- → H removed by solvent H_2O molecules to form H_3O^+

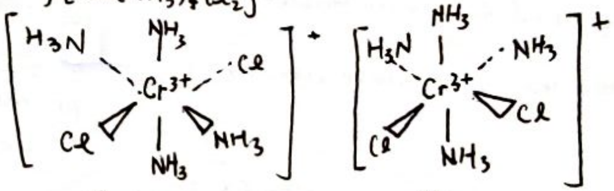


- → water ligands deprotonated by water molecules.
- → EQN
  $[M(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5(OH)]^+ + H_3O^+$
- → Theoretically : all H_2O can become OH^- & ppt out
  $[M(H_2O)_4(OH)_2]$ or $M(OH)_2$ → OH balances +ve charge

→ GEOMETRICAL

↳ same molecular, same structural formulae, but diff spatial arrangements of ligands around central metal ion

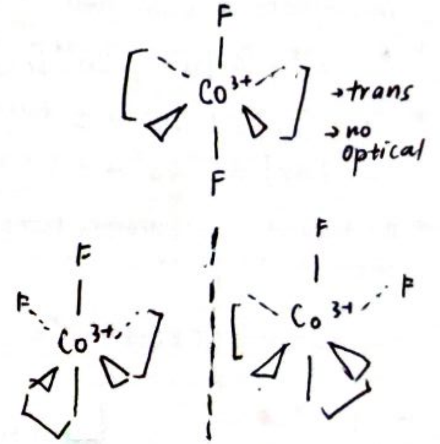
→ Eg $[Cr(NH_3)_4Cl_2]^+$



trans
↳ non-polar

cis
↳ polar

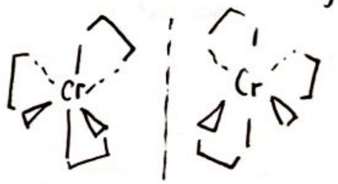
→ If have bi & mono ,



→ trans
→ no optical

→ OPTICAL

→ only or similar $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$ & $[Cr(C_2O_4)_3]^{3-}$



All mono → cis trans

All bi → optical

mix → can have both

	Cobalt (II) ~~(HYDROLYSIS)~~ (also Ni) ~~REACTION W/ NaOH(aq)~~	Copper (II)	Chromium (III) follow charge	Iron (III) ~~Manganese~~	Iron (II)
w/ NaOH(aq) hydrolysis	$[Co(H_2O)_6]^{2+}(aq) + 2OH^-(aq)$ pink ↓ $[Co(OH)_2(H_2O)_4](s) + 2H_2O$ blue ppt (insoluble in excess) ↳ or $Co(OH)_2$ * non amphoteric stops when hydroxide salt is formed OH⁻ and NH_3 remove H^+ products same.	$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq)$ blue ↓ $[Cu(OH_2)(H_2O)_4]_s + 2H_2O(l)$ pale blue ppt (insoluble in excess) ↳ or $Cu(OH)_2$ further protons removed	$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-$ violet ↓ $[Cr(OH)_3(H_2O)_3]_s + 3H_2O$ green ppt SOLUBLE in excess amphoteric ↓ $[Cr(OH)_3(H_2O)_3]_s + 3H^+(aq)$ green ↓ $[Cr(H_2O)_6]^{3+}(aq)$ violet reversible (excess alkali) deprotonate $[Cr(OH)_3(H_2O)_3]_s + 3OH^-(aq)$ green ↓ $[Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$ green	$[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq)$ yellow ↓ $[Fe(OH)_3(H_2O)_3]_s + 3H_2O(l)$ red brown ppt insoluble	$[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq)$ pale green ↓ $[Fe(OH)_2(H_2O)_4]_s + 2H_2O(l)$ dirty green ppt insoluble oxidation to Fe^{3+} ↓ $[Fe(OH)_2(H_2O)_4] + OH^-(aq)$ dirty green ↓ $[Fe(OH)_3(H_2O)_3] + H_2O + e^-$ rusty brown
w/ NH_3(aq) hydrolysis	$[Co(H_2O)_6]^{2+} + 2NH_3(aq)$ pink ↓ $[Co(OH)_2(H_2O)_4](s) + 2NH_4^+$ blue ppt	$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq)$ blue ↓ $[Cu(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)$ pale blue	$[Cr(H_2O)_6]^{3+}(aq) + 3NH_3(aq)$ violet ↓ $[Cr(OH)_3(H_2O)_3](s) + 3NH_4^+(aq)$ green * ammonia weak base ∴ no anion formed.	$[Fe(H_2O)_6]^{3+}(aq) + 3NH_3(aq)$ yellow ↓ $[Fe(OH)_3(H_2O)_3](s) + 3NH_4^+(aq)$ red brown ppt insoluble	$[Fe(H_2O)_6]^{2+}(aq) + 2NH_3(aq)$ pale green ↓ $[Fe(OH)_2(H_2O)_4](s) + 2NH_4^+$ dirty green ppt insoluble
w/ EXCESS NH_3(aq) ligand substitution *CCN*	$[Co(OH)_2(H_2O)_4](s) + 6NH_3$ blue ↓ $[Co(NH_3)_6]^{2+}(aq) + 4H_2O + 2OH^-$ yellow / brown then oxidised by air ↓ $[Co(NH_3)_6]^{2+}(aq) \rightarrow [Co(NH_3)_6]^{3+}(aq) + e^-$ yellow brown / red brown can combine eqn	$[Cu(OH)_2(H_2O)_4](s) + 4NH_3(aq)$ pale blue ↓ $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-$ deep blue * partial	$[Cr(OH)_3(H_2O)_3](s) + 6NH_3(aq)$ green ↓ $[Cr(NH_3)_6]^{3+}(aq) + 3H_2O(l) + 3OH^-$ green	—	—

	Cobalt (II)	Copper (II)	Chromium (III)	Iron (III)	Iron (II)
eaction w/ hloride ions (conc HCl) Ligand Substitutio	$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$ pink ↓ $[CoCl_4]^{2-}(aq) + 6H_2O(l)$ blue → Cl^- ligand larger than H_2O & are charged → shape = tetrahedral ↳ less repulsion between ligands ∴ [illegible] ↑ stable → excess H_2O reverses reaction	$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$ blue ↓ $[CuCl_4]^{2-}(aq) + 6H_2O(l)$ yellow → same	—	—	—
Reaction with I^- Redox	—	$2Cu^{2+}(aq) + 4I^- \rightarrow 2CuI(s) + I_2(aq)$ blue off-white ppt	—	—	—
Oxidation $(Cr(III) \rightarrow Cr(VI))$ H_2O_2 in alkali	—	—	$2Cr^{3+}(aq) + 3H_2O_2(l) + 10OH^-(aq)$ green ↓ $2CrO_4^{2-}(aq) + 8H_2O(l)$ yellow	—	—
Reduction $(Cr(III) \rightarrow Cr(II))$ zinc in HCl	—	—	$2[Cr(H_2O)_6]^{3+}(aq) + Zn(s)$ green ↓ $2[Cr(H_2O)_6]^{2+}(aq) + Zn^{2+}$ blue	—	—
Reaction w/ thiocyanate ions (SCN^-) Ligand Substitution				* NOT reduction, just overall charge of complex ion changed due to ligand $[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq)$ yellow ↓ $[Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$ blood-red colour → use as very sensitive reagent to distinguish Fe^{2+} & Fe^{3+} → No reaction w/ Fe^{2+}	

TRANSITION METALS

- For amphoteric hydroxides, $Al(OH)_3$ (ppt), $Cr(OH)_3$ & $Zn(OH)_2$, IF base strong, further protons are removed & ppt dissolves as soluble anionic complexes.
  - $[M(OH)_6]^{3-}(aq)$ ∴ Al has no ppt in excess NaOH.
- very weak bases → H_2O → remove few H^+
  - weak bases → NH_3, CO_3^{2-} → remove H^+ until ppt
  - strong bases → OH^- → can remove all H^+

LIGAND SUBSTITUTION REACTIONS

- **OCCURS STEP-WISE**
  - depends on ligand strength & conc.
  - Eg with aq NH_3 in excess,

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

- BUT FOR COPPER:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

  - ↳ only 4 ligands substituted
  - ↳ Cu (& Zn) most protons ∴ bind strongly to O_2.

- **REVERSIBLE**

$$\underset{\text{PINK}}{[Co(H_2O)_6]^{2+}} + 4Cl^- \underset{}{\overset{(+\text{conc } HCl) \rightarrow}{\rightleftharpoons}} \underset{\text{BLUE}}{[CoCl_4]^{2-}} + 6H_2O$$

← (+ excess)

- **EFFECT ON CO-ORDINATION NO. + SHAPE**
  - Cl^- larger than H_2O $\underset{\text{octahedral}}{[Co(H_2O)_6]^{2+}}$, $\underset{\text{tetrahedral}}{[CoCl_4]^{2-}}$
  - H_2O & NH_3 = similar size, both neutral ∴ no change in co-ordination no. & shape.
- **CHANGES COLOUR**

$$\text{Eg } \underset{\text{blue}}{[Cu(H_2O)_6]^{2+}} + 4NH_3 \rightleftharpoons \underset{\text{deep blue}}{[Cu(NH_3)_4(H_2O)_2]^{2+}} + 4H_2O$$

(diff splitting of d orbitals)

COPPER (I)

- unstable
- goes through disproportionation
- $Cu^+(aq) + e^- \rightarrow Cu(s)$ $E^\circ = +0.52V$
  - $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $E^\circ = +0.15V$
  - overall $2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ $E^\circ = +0.37V$
- can be stabilised by forming $[Cu(NH_3)_2]^+$, $[Cu(CN)_2]^-$

CHROMIUM (VI)

- can form → dichromate (VI) ions
  - stable in acid ← $Cr_2O_7^{2-}$ orange solution
  - → chromate (VI) ions
  - stable in alkali ← CrO_4^{2-} yellow solution
- $Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H_2O(l)$
- $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$
  - * NOT redox.
- chromium (VI) have highest oxi state ∴ oxi agents.
- $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+} + 7H_2O(l)$ $E^\circ = +1.33V$
- E° value ↓ than Cl_2 ∴ can be used in presence of Cl^- ions (cannot $Cl^- \rightarrow Cl_2$)
- reduced by zinc in HCl (like Cr(III) → Cr(II))

CHROMIUM (II)

- unstable ∴ stabilised by forming complex w/ CH_3COO^-
- $2[Cr(H_2O)_6]^{2+}_{(aq)} + 4CH_3COO^-_{(aq)} \rightarrow [Cr_2((H_3COO)_4(H_2O)_2](s) + 10H_2O(l)$
- ligand substitution

MANGANESE

- Mn(VII) exists as MnO_4^- (purple) permanganate ions
- oxi agent in acidic / alkaline
- (acid) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow \underset{(+2)}{Mn^{2+}}(aq) + 4H_2O(l)$
- $MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow \underset{(+4)}{MnO_2}(s) + 4OH^-(aq)$
- In volumetric analysis, must use H_2SO_4 ∵ can oxidise Cl^- ($Cl^- \rightarrow Cl_2$)

VANADIUM

- 4 oxi states (common)
- diff oxistates observed when ammonium vanadate (V) reduced using zinc + conc HCl

can appear green

(V)	$VO_3^-(s)$ $VO_2^+(aq)$ } + conc. HCl	white yellow	young
(IV)	VO^{2+}	blue	baboon
(III)	V^{3+}	green	grows
(II)	V^{2+}	violet	violet

- several distinct colour changes occur
- can be explained using E^θ values.
  - → Eg (oxi) $Zn^{2+} + 2e^- \rightarrow Zn$ -0.76 ← 1st step Zn oxidise, then V oxidise as go down
  - (red) $2VO_3^- + 4H^+ + 2e^- \rightarrow 2VO^{2+} + 2H_2O$ $+1.00$

$$2VO_3^- + 8H^+ + Zn \rightarrow 2VO^{2+} + 4H_2O + Zn^{2+}$$

$$E^\theta_{cell} = 1.00 - (-0.76) = \underline{\underline{+1.76}} \checkmark$$

* $V^{2+} \rightarrow V$ cannot $E^\theta_{cell} = -1.2(-0.76) = \underline{\underline{-ve}}$ ∴ ×

TRANSITION METALS

USES OF TRANSITION METALS

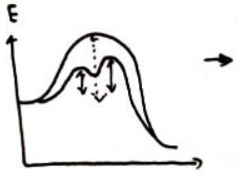
- (Iron)→catalyst, structural material
- (copper)→electrical conductor, decorative metal
- (copper (I) chloride)→photochromic glass.

$$\underset{\text{clear}}{CuCl + AgCl} \rightleftharpoons CuCl_2 + \underset{\text{silver}}{Ag}$$

- (chromium)→alloyed w/ iron → stainless steel, resist corrosion
- (vanadium (V) oxide, V_2O_6)→catalyst in Contact process.

TRANSITION METALS AS HETEROGENEOUS CATALYSTS

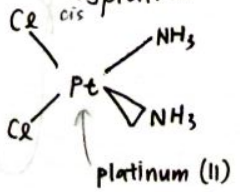
- do not alter $\Delta G, \Delta H, \Delta S$, just Ea.
- can be separated from products.
- adsorbtion of reactants onto surface can:
  - → concentrate reactants (bring the closer tgt than in gas form, collision ↑)
  - → weaken bonds in molecule
  - → position molecule in favourable orientation.



- choice of catalyst influences products.
  - $\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[\text{(copper)}]{} \underset{\text{ethanal}}{CH_3CHO} + H_2$
    - ↳ dehydrogenation / oxidation
  - $\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[\text{(alumina } Al_2O_3)]{} \underset{\text{ethene}}{C_2H_4} + H_2O$
    - ↳ dehydration.
- CO poisons iron catalyst
- lead poisons metal catalysts in catalytic converter.

CHEMOTHERAPY

- cisplatin



- square planar
- prevents cell division by binding w/ DNA
- But prevents normal cells from dividing
  - ∴ immune system ↓, infection, kidney damage.

LIGAND EXCHANGE IN HAEMOGLOBIN

- Ligands, CO forms dative covalent bond w/ iron atom more readily than O_2
  - ↳ Iron – CO STRONGER than Iron-O_2 bond.
  - ∴ CO displaces Oxygen in HbO_2

$$HbO_2 + CO \rightarrow HbCO + O_2$$

- treatment = pure oxygen
  - ↳ displaces CO by mass action effect.

TRANSITION METALS AS HOMOGENOUS CATALYSTS

- proceeds via an intermediate species formed from reactant + catalyst, which then reacts further and regenerates catalyst.
- Eg esterfication

$$X + Y \xrightarrow{H^+} \text{products}$$
$$X + \cancel{H^+} \rightarrow \cancel{HX^+}$$
$$\cancel{HX^+} + Y \rightarrow \text{products} + \cancel{H^+}$$

- Eg I^- + peroxodisulphate ions

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe^{2+}} I_2 + 2SO_4^{2-}$$
$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$
$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

  - → transition metal compounds have ability to vary their oxi states ∴ can be catalysts.
  - → involves 2 -ve ions ∴ repulsion
- autocatalysis in manganate (VII) + ethandioate

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \xrightarrow{Mn^{2+}} 2Mn^{2+} + 8H_2O + 10CO_2$$
$$4Mn^{2+} + 4MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O \quad \}\times 2$$
$$2Mn^{3+} + C_2O_4^{2-} \rightarrow 2CO_2 + 2Mn^{2+} \quad \}\times 5$$

STABILITY CONSTANT, Kstab

↳ equilibrium constants for the formation of complex ions in an aqueous solution

$$Cu(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CuCl_4^{2-}(aq) + 6H_2O$$

$$K_c = \frac{[CuCl_4^{2-}][H_2O]}{[Cu(H_2O)_6^{2+}][Cl^-]^4}$$

[H₂O] → constant due to large amount.

$$\therefore K_{stab} = \frac{K_c}{[H_2O]} = \frac{[CuCl_4^{2-}]}{[Cu(H_2O)_6^{2+}][Cl^-]^4}$$

- Kstab ↑ stability of complex ion ↑ compared w/ complex ion w/ H_2O ligands.
- $[Cu(NH_3)_4(H_2O)_2]^{2+} \rightarrow K_{stab} = 1.3 \times 10^{13}\ dm^{12}\ mol^{-4}$ ← more stable
- $[CuCl_4^{2-}] \rightarrow K_{stab} = 4.0 \times 10^{5}\ dm^{12}\ mol^{-4}$

∴ NH_3 will replace Cl^- ligands if conc. same

COMPLEX IONS & ENTROPY

- when bidentate ligand replace monodentate
  - ↳ entropy ↑ ∵ no. of molecules ↑
  - (need more of transition metal to "accomodate bidentate)
- when poly dentate replace monodentate
  - ↳ entropy ↑↑
- stability

polydentate ligands > bi > mono