

TRANSITION METALS

TRANSITION **METALS**

CHEM 5

Updated 30 January 2015

Coordination number 4:

tetrahedral and square

planar complex

Coordinatio

6:

Octahedral

dentate

actior ed in F alysis

Part I

LATEST: Define transition metal, ligand, complex ion, unidentate, bidentate, hexaden Lewis acid, Lewis base. State the chemical properties of transition elements. \rightarrow

linear complexes.

COMPLEXES



LIGANDS



REACTIONS

	Ligands are Lewis bases: they are electron pair donors. Transition metal ions are Lewis acids: they are electron pair acceptors	Redox reactions are reactions where transition metals change their oxidation states	Manganate reduction reaction: $MnO_{4} + 5e^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_{2}O$	$\begin{tabular}{ c c } \hline Fe^{tt}Ot, & Fe^{tt}OH), \\ \hline cr(th) & cr(th) \\ \hline Chromate reduction \\ reaction: Cr_2O_7^{2-} + \\ 6e^- + 14H^+ & 2Cr^{3+} \\ + 7H_2O \end{tabular}$	Fr
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CASE STUDIES: Cu, Fe, Cr, Co

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SUMMARY OF THE WEEK

THE BASICS

Last updated I hour ago

Transition metals are d-block elements and at A2 you study mainly the elements found in Period 4 of the Periodic table, titanium to copper.

By definition, transition elements are elements that form at least one ion with a partially filled d-subshell. This explains why scandium and zinc are d-block elements but not transition elements:

Scandium [Ar]3d¹4s² forms a Sc³⁺ ion only: [Ar]3d⁰4s⁰ Zinc [Ar]3d¹⁰4s² forms a Zn²⁺ ion only: [Ar]3d¹⁰4s⁰ In both cases, the definition of a transition metal has not been met. (* remember that the 4s electrons are removed first)

All other Period 4 d-block elements form at least one ion with a partially filled d-subshell:

I	22	23	24	25	26	27	28	29
	Ti	V	Cr	Mn	Fe	Со	Ni	Cu
ł	[Ar]3d ² 4s ²	[Ar]3d ³ 4s ²	[Ar] 3d ⁵ 4s ¹	[Ar]3d ⁵ 4s ²	[Ar]3d ⁶ 4s ²	[Ar]3d ⁷ 4s ²	[Ar]3d ⁸ 4s ²	[Ar]3d ¹⁰ 4s ¹
	Ti³+	V ³⁺	Cr ²⁺	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺
2+	3d ¹	3d ²	3d ⁴	3d⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹

Transition metal (chemical) properties:

Most transition metals have compounds with variable oxidation states. At least one of these compounds is coloured. Many transition metals (or their compounds) act as catalysts due the their ability to change oxidation states. Transition metals also form complex ions with ligands

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Part II

Redox Reactions

LATEST: Describe the redox behaviour in transition elements.

PERMANGANATE

Updated 31 January 2015

 \rightarrow

0.325g of an iron tablet is dissolved in 25cm³ of acid. 2.5cm³ of the resulting solution was titrated with 0.002moldm⁻³ potassium permanganate solution, and 12.10cm³ of the permanganate solution was used. Find the % mass of iron in the tablet.



 $5Fe^{2+} + MnO_4^{-+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ Moles $MnO_4^{-} = 0.002 \times 12.10/1000 = 2.42 \times 10^{-5}$ Moles Fe^{2+} in $2.5cm^3 = 5 \times 2.42 \times 10^{-5} = 1.21 \times 10^{-4}$ Moles Fe^{2+} in $25cm^3 = 10 \times 1.21 \times 10^{-4} = 1.21 \times 10^{-3}$

Mn2+
IVITI
Pale
pink

Mass iron = moles x molar mass = 1.21x10⁻³ x 55.8 = 0.0675g % mass = 0.0675/0.325 = 0.2077 = 20.77%

DICHROMATE

A solution containing aqueous $Cr_2O_7^2$ ions was titrated against 25cm³ of 0.05moldm-³ Fe²⁺ ions in acid solution. The volume of the dichromate solution required to reach the endpoint was 12.30cm³. What was the concentration of the dichromate solution?



 $\begin{array}{l} 6\text{Fe}^{2+}+\text{Cr}_2\text{O}_7^{2-}+14\text{H}^+ \rightarrow 6\text{Fe}^{3+}+14\text{H}_2\text{O}+2\text{Cr}^{3+}\\ \text{Moles}\ \text{Fe}^{2+}=0.05 \times 25/1000=0.00125\\ \text{Moles}\ \text{Cr}_2\text{O}_7^{2-}=0.00125/6=2.083 \times 10^{-4} \end{array}$



Concentration = moles x 1000/volume = 2.083x10⁻⁴ x 1000/12.30 = 0.017moldm⁻³

THIOSULFATE

0.6g of bronze is dissolved in nitric acid to form a solution that contains Cu²⁺ ions. After neutralisation, the solution is reacted with iodide ions to form iodine. The iodine is titrated with 0.15moldm⁻³ sodium thiosulfate. 22.30cm³ are required. What is the % of copper in the bronze?



OTHER HALF EQUATIONS: $C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$; $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

CASE STUDIES: Cu, Fe, Cr, Co

CATALVEIS & COLODIMETRY

SUMMARY OF THE WEEK

AN OVERVIEW

Last updated I hour ago



Transition metals have variable oxidation states and each oxidation state has a characteristic colour. This allows chemists to use redox titrations in analysis.

The most important redox reactions at A2 are those that take place between permanganate ions and iron(II) ions, dichromate ions and iron(II) ions, copper(II), iodide and thiosulfate ions.

Permanganate titrations:

 MnO_4^- is reduced by Fe^{2+} under acidic conditions (H_2SO_4 rather than HCl as otherwise Cl_2 would be released as the HCl reacts with the oxidising agent MnO_4^-). The reaction is self-indicating as the purple MnO_4^- is reacted to pink Mn^{2+} ions which means the colourless Fe^{2+} solution changes to pale pink at the end point.

Dichromate titration:

 $Cr_2O_7^{2-}$ is reduced by Fe²⁺ under acidic conditions (H₂SO₄ again for the same reasons as above). Cr³⁺ ions are produced.



Thiosulfate titration:

Firstly, iodide ions are added to the ion under investigation (i.e. Cu^{2+}). Iodine and a white Cul precipitate are produced. The mixture of I_2 and Cul is then titrated against $S_2O_3^{2-}$. I_2 is reduced to I^- and the colour changes from brown to pale yellow. Starch is added and a black colour forms due to the remaining I_2 . When the colour disappears, the endpoint is reached.



the base CO_3 is added, $CUCO_{3(s)}$ is to



ADDITIONAL KNOWLEDCE

 $[Fe(H_2O)_6]^{3+} + H_2O \implies Fe(H_2O)_5(OH)]^{2+} + H_3O^+$



ADDITIONAL KNOWLEDGE

 $Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$



EVAM OUESTIONS

TRANSITION METALS

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Part VII

LATEST: Give examples of heterogeneous and homogeneous catalysts and describe autocatalysis. Explain why transition metal compounds are coloured. Describe colorimetry \rightarrow

COLOURED IONS Updated | February 2015 In an isolated d-As soon as ligands The gap between the The colour of block element, the bond to the central orbitals depends on 个个 transition metal ion, the d-orbitals the type of ligand, 5 d-orbitals have compounds is are 'split': number of coordinate the same energy. due to d-orbital bonds and oxidation splitting. state of the central ion. **D-ORBITAL SPLITTING** Electrons absorb energy The energy gap and Examples: \mathbb{T} from the visible region of the frequency of the the spectrum to move to light absorbed are $VO_2^+ =$ yellow a higher energy d-orbital. We observe the related according to $VO^{2+} = Blue$ transmitted colour. E.g. V^{3+} = green 个个 the equation: a solution appears red V^{2+} = violet because it absorbs light h= Planck's constant; v= frequency in the blue region. COLORIMETRY Light detecto The method Colorimetry The colorimeter measures the intensity of the colour in the This is a method used to determine the formula liquid by passing filtered light through the sample. The filter of a complex ion by finding the central ion to is of the colour that is absorbed by the solution. ligand ratio. The maximum absorbance is taken from the graph. The Solutions containing the metal ion and ligand are molar ratio of the central ion and ligands can then be mixed in varying proportions. When mixed in the calculated from the volumes and concentrations of both same ratio as in the complex, the solution will solutions at the maximum absorbance. absorb most light. **ADDITIONAL KNOWLEDGE**

EXAM QUESTIONS

SUMMARY OF THE WEEK

Last updated I hour ago

Heterogeneous catalysts

A catalyst that is in a different phase from the reactants. (3 steps: Adsorption, Reaction, Desorption). Catalysts are usually spread over a ceramic support surface to reduce the cost and maximise the surface area. Catalysts can become coated with impurities and are 'poisoned' as a result. This reduces the efficiency of the catalysts.

CATALYSIS &

COLORIMETRY

Examples of heterogeneous catalysts:

Fe in the Haber process $N_2 + 3H_2 \rightleftharpoons 2NH_3$

 $\begin{array}{l} \textbf{V}_2\textbf{O}_5 \text{ in the Contact process } SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3 \\ \text{Step I: } V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3 \\ \text{Step 2: } V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5 \end{array}$

Ni in hydrogenation of oils (adding H_2 to a C=C bond)

 $\begin{array}{l} \textbf{Cr}_2\textbf{O}_3 \text{ in production of methanol from CO and } H_2 \\ \text{Step I: CH}_4 + H_2O \rightarrow \text{CO} + 3H_2 \\ \text{Step 2: CO} + 2H_2 \rightarrow \text{CH}_3\text{OH} \end{array}$

Homogeneous catalysts:

A catalyst that is in the same phase as the reactants. The catalysts reacts with the reactants to form an intermediate state with a lower activation energy. The catalyst is regenerated at the end of the reaction:

$$\begin{split} &S_2O_8^{2-} + \underline{2Fe^{2+}} \rightarrow 2SO_4^{2-} + \underline{2Fe^{3+}}; 2Fe^{3+} + 2I^- \rightarrow \underline{2Fe^{2+}} + I_2 \\ \underline{Autocatalysis:} \ 2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2 \\ \underline{4Mn^{2+}} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O \\ 2Mn^{3+} + C_2O_4^{2-} \rightarrow Mn^{2+} + 2CO_2 \end{split}$$

The reaction is slow at the start (both ions are negative) but speeds up once the catalyst Mn^{2+} is produced during the reaction.

TEGT

TRANSITION METALS

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Part VIII

LATEST: Describe chelation. Give examples of square planar complex ions. Describe summary of THE WEEK action of cis-platin on cancer cells. Describe the amphoteric nature of $AI(OH)_3$.

CHELATION



EVAM



Ouestion



State 3 different features of transition metal complexes that change the value of ΔE .

3 marks

Answer



Oxidation state of metal, type of ligand, size of ligand, type of central metal ion, shape of complex ion.



Transition metals



Give the meaning of the term autocatalysed.

🕨 l mark

Answer



The catalyst is a reaction product.



Transition metals



Give the general property that allows transition metals to act as catalysts.

l mark



Answer



They have variable oxidation states.



Transition metals



Explain the meaning of the terms ligand and bidentate.

> 2 marks

Answer



A ligand is an electron pair donor. A bidentate ligand donates two pairs of electrons from two different atoms.





Ouestion



List 4 transition metal shapes and give an example for each.

4 marks

 $([CuCl_4]^{2-}),$

(any aqua



 $([Ag(NH_3)_2]^+,$ Linear square planar (cis-platin), tetrahedral octrahedral complex)



Transition metals

Question



Why can s-block elements not act as catalysts?

l mark

Answer



Because they only exist in one oxidation state.



Transition metals



In terms of bonding, define a complex.

I mark



Answer



metal ion A central surrounded by ligands which form coordinate bonds with the metal ion.



Suggest what is done to heterogeneous catalysts increase their efficiency. 2 marks

Answer



Spread the catalyst over support base а to increase the surface area of the catalyst.









State and explain one risk associated with using cisplatin as an anticancer drug.

2 marks

Answer



It binds to normal cells and kills them. This can lead to side effects such as hair loss.



Transition metals

Question



What is the meaning of the symbols ΔE and h?

2 marks

Answer



Energy absorbed and Planck's constant.



A 2 CHEMISTRY					
Transition metals					
Ouestion	How can poisoning of a catalyst be minimised?				
	I mark				
Answer z c	Remove impurities from the reactants.				
A 2	CHEMISTRY				
Transitio	n metals				
Question	In terms of electrons, explain why CoSO₄ is red in colour.				
	3 marks				
Answer z z c	Blue light is absorbed when an electron moves to a higher energy d- orbital. Red light is transmitted which is what we observe				





l mark number of coordinate bonds formed to a central metal ion. CHEMISTRY What can you observe when aqueous ammonia with aqueous reacts Fe(III)?

coordination

Yellow solution to brown, gelatinous precipitate which is insoluble in excess ammonia.

2 marks



Transition metals



Explain why transition metals which adsorb a) strongly or b) weakly are not usually good catalysts.

2 marks

Answer



blocked/ products cannot desorb.

a) The active site will be

b) Reactant bonds will not weaken.



Transition metals

Question



Why are transition metal compounds coloured?

2 marks

Answer



Electrons absorb light in the visible region of the spectrum to transfer/excite to a high energy d-orbital.



Transition metals



Answer

When monodentate ligands are substituted by bior multidentate ligands to give more stable complex ions due to an increase in entropy.

2 marks



I mark

Answer



electron An pair acceptor. (Lewis base is an electron pair donor)



Answer



A shared pair of electrons which has been donated by one atom to form a covalent bond.





























