Spontaneous Redox Reactions 3

A Level

Essential Pre-Uni Chemistry L3.3

	Reduction	$E^\ominus$ / V		Reduction	$E^\ominus$ / V
1	$\mathrm{As(V) \longrightarrow As(III)}$	$+0.56$	7	$\mathrm{Cr(VI) \longrightarrow Cr(III)}$	$+1.33$
2	$\mathrm{As(III) \longrightarrow As}$	$+0.25$	8	$\mathrm{Cr(III) \longrightarrow Cr(II)}$	-0.41
3	$\mathrm{As \longrightarrow As(-III)}$	-0.23	9	$\mathrm{Cr(II) \longrightarrow Cr}$	-0.74
4	$\mathrm{Mn(VII) \longrightarrow Mn(IV)}$	$+1.70$	10	$\mathrm{I(VII) \longrightarrow I(V)}$	$+1.60$
5	$\mathrm{Mn(IV) \longrightarrow Mn(II)}$	$+1.23$	11	$\mathrm{I(V) \longrightarrow I}$	$+1.19$
6	$\mathrm{Mn(II) \longrightarrow Mn}$	-1.19	12	$\mathrm{I \longrightarrow I(-I)}$	$+0.54$

Some reduction half-equations involving iron are shown below:

$$\mathrm{FeO_4^{2-} + 6\,H^+ + 3\,e^- \longrightarrow Fe^{3+}} \qquad E^\ominus = +2.20\,\mathrm{V}$$

$$\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}} \qquad E^\ominus = +0.77\,\mathrm{V}$$

$$\mathrm{Fe^{2+} + 2\,e^- \longrightarrow Fe} \qquad E^\ominus = -0.44\,\mathrm{V}$$

Part A Oxidising $\mathrm{Mn(IV)}$

Give the oxidation state of iron capable of oxidising $\mathrm{Mn(IV)}$.

Part B Highest oxidation states

For each of the four elements listed, select the highest oxidation state that could be attained using Fe^{3+} as the oxidising agent in aqueous acid: As, Cr, Mn, I

As

Cr

Mn

I

Part C Lowest oxidation states

For each of the three elements listed, select the lowest oxidation state capable of oxidising Fe^{2+} in aqueous acid: Cr, Mn, I

Cr

Mn

I

Part D Final oxidation states

For each of the four elements listed, select the final oxidation state spontaneously reached via reduction of a higher state on exposure to metallic iron: As, Cr, Mn, I

As

Cr

Mn

I

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Predicting Reactivity

A Level

Standard electrode potentials can be used to predict how reactive different chemical species are.

Part A Reduction to metal

The metal ions below have different standard reduction potentials for the reductions to their neutral metal form. Which of the chemical species present is the best oxidising agent and which is the best reducing agent?

$$\mathrm{Ag^+ + e^- \longrightarrow Ag} \qquad (E^\ominus = +0.80\,\mathrm{V})$$

$$\mathrm{Fe^{2+} + 2\,e^- \longrightarrow Fe} \qquad (E^\ominus = -0.45\,\mathrm{V})$$

$$\mathrm{Zn^{2+} + 2\,e^- \longrightarrow Zn} \qquad (E^\ominus = -0.76\,\mathrm{V})$$

$$\mathrm{Cu^{2+} + 2\,e^- \longrightarrow Cu} \qquad (E^\ominus = +0.34\,\mathrm{V})$$

Strongest oxidising agent: [ ]

Strongest reducing agent: [ ]

Items:

[Zn] [Ag] [Fe] [$\mathrm{Zn^{2+}}$] [$\mathrm{Ag^+}$] [$\mathrm{Fe^{2+}}$] [Cu] [$\mathrm{Cu^{2+}}$]

Part B Standard cell potential

What is the standard cell potential for a cell which has the following conventional cell reaction? Give your answer to 2 decimal places.

$$\mathrm{Fe^{2+} + 2\,Ag \longrightarrow Fe + 2\,Ag^+}$$

Part C Spontaneous direction

The standard electrode potential calculated is [ ]. This means the reaction is spontaneous in the [ ] direction at standard conditions.

Items:

reverse **forward** **negative** **positive**

Created for isaacphysics.org by Andrea Chlebikova

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Ammonia Decomposition

A Level

C C C

In an experiment, the decomposition of gaseous ammonia to $\mathrm{N_2}$ and $\mathrm{H_2}$ on a hot tungsten wire was studied by monitoring the change in pressure with time. The rate equation for this reaction may be written in terms of either the concentration or the partial pressure of ammonia. In terms of the partial pressure of ammonia, $p_{\mathrm{NH_3}}$, it is:

$$\mathrm{rate} = -k(p_{\mathrm{NH_3}})^{\alpha},$$

where α is the order of the reaction and k is the rate constant.

At the start of the reaction, the only gas present was ammonia at an initial pressure of $200\,\mathrm{mmHg}$. The table below shows how the total pressure varied with time.

Time / s	**Total pressure /** mmHg
100	214
200	227
300	238
400	249
500	259
600	270
800	292

Part A Equation

Write a balanced equation, including state symbols, for the decomposition of one mole of ammonia.

Part B Pressure vs concentration

Using the ideal gas law, we can show that pressure is directly proportional to concentration at constant temperature. What is the proportionality constant we need to multiply concentration by to get the pressure?

The following symbols may be useful: `R, T, V, n, p`

Part C Total pressure

The initial partial pressure of ammonia is $p_0\,\mathrm{mmHg}$. After a time t it is $(p_0 - x)\,\mathrm{mmHg}$. Find an expression for the *total* pressure of reactants and products, p_T, at time t, expressed in mmHg (don't include the unit in your expression).

The following symbols may be useful: `p_0, t, x`

Part D Partial pressure

Find an expression for the *partial pressure of ammonia* at time t as a function of p_0 and p_T, expressed in mmHg (don't include the unit in your expression).

The following symbols may be useful: `p_0, p_T`

Part E Graph

Which of the following statements are true about the graph of the partial pressure of ammonia against time?

- [ ] It appears to be approximately a straight line.
- [ ] It appears to be approximately a parabola
- [ ] It appears to be approximately S-shaped
- [ ] It has a positive gradient throughout
- [ ] It has zero gradient throughout
- [ ] It has a negative gradient throughout
- [ ] It has both a positive and a negative gradient over different intervals.
- [ ] The graph is steepest at around $t = 400\,\mathrm{s}$
- [ ] The graph gets steeper at higher times

Part F Order

What is the order of the reaction, α?

Part G Rate constant

What is the rate constant of the reaction? Give your answer to 2 s.f.

Adapted with permission from OCR, STEP Chemistry, Jun 1999, Question 2

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Elementary Steps

A Level
C C C

An **elementary step** of a reaction mechanism is a step that is unimolecular (involving a single atom, molecule or ion of a substance as the reagent), or a step that only involves a single collision between all the species listed as its reagents. In general, reactions can proceed by several elementary steps occurring in succession, or by a more complicated network of elementary steps. Such a network may feature both the forward and reverse reactions of the same step, in some cases, or side reactions that may or may not produce the main products, which complicates the kinetic behaviour of the overall reaction.

The rate equation for an elementary step can be written down without any additional knowledge, as the order of reactants is simply equal to the stoichiometric coefficient in the equation. This means, in particular, that we cannot simply multiply an elementary step arbitrarily. While this would leave the equation balanced, it would represent a different elementary step! We also **cannot** cancel species that appear on both sides of the equation.

Part A Two elementary steps

Consider the elementary steps $\mathrm{A} \longrightarrow \mathrm{B}$ and $2\,\mathrm{A} \longrightarrow \mathrm{A} + \mathrm{B}$ respectively. Which of the following statements are correct?

- [ ] The equations of the elementary steps are both balanced.
- [ ] The two elementary steps are equivalent.
- [ ] The elementary step $\mathrm{A} \longrightarrow \mathrm{B}$ is unimolecular.
- [ ] The two elementary steps would have the same rate law.

Part B Rate-determining step

It is common to want to simplify the kinetics of multi-step reactions. Sometimes, it is possible to identify a "rate-determining step", and the rate of the overall reaction can be considered to equal the rate of the rate-determining step.

If the first step in the reaction sequence $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \longrightarrow \mathrm{D}$ can be considered rate-determining under a certain set of conditions, what rate law would you expect to describe the rate of the overall reaction? Use r to denote the rate, k for the rate constant, and lower-case letters to denote the concentrations of the species (e.g. $[\mathrm{A}] = a$).

The following symbols may be useful: `a, b, c, d, k, r`

Part C Relative rates

Continuing with the previous set-up with the first step in the reaction sequence $\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} \longrightarrow \mathrm{D}$ considered rate-determining, how would you expect the rate of the first step, r_1, to compare to the rate of the second step, r_2?

The following symbols may be useful: `r_1, r_2`

Created for isaacphysics.org by Andrea Chlebikova

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

pH in Ester Hydrolysis

A Level

The hydrolysis of an ester can be carried out in both alkaline and acidic conditions.

Part A Equations

Fill in the gaps to complete the reaction equations for hydrolysis of ethyl ethanoate under acidic and alkaline conditions respectively.

$$\mathrm{CH_3C(=O)OCH_2CH_3} + \mathrm{H_2O} \xrightarrow{\text{acid}} \square + \square$$

$$\mathrm{CH_3C(=O)OCH_2CH_3} + \mathrm{NaOH} \xrightarrow{\text{alkali}} \square + \square$$

Items:

$\mathrm{H_2O}$ $\mathrm{CH_3OH}$ $\mathrm{CH_3CH_2OH}$ HCOOH $\mathrm{CH_3COOH}$ HCOONa $\mathrm{CH_3COONa}$

Part B pH rate profile

A study of the rate of hydrolysis of ethyl ethanoate in buffered solutions gave the following pH rate profile:

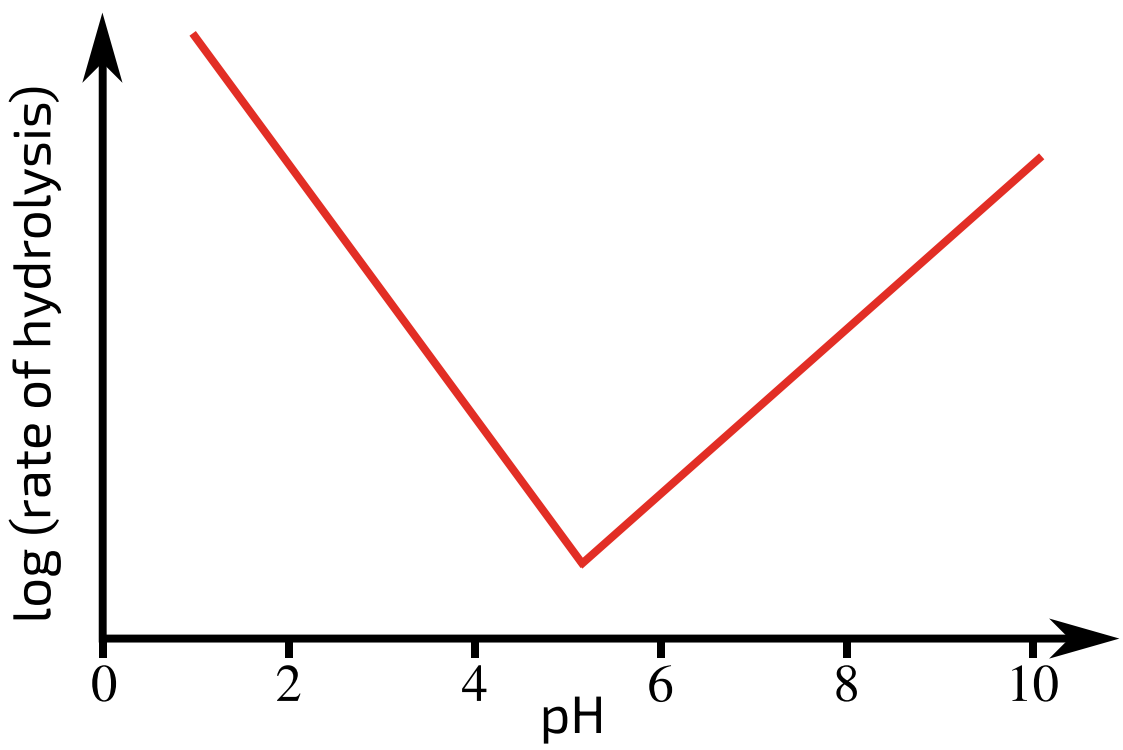


Figure 1: pH rate profile for ester hydrolysis

Which of the following statements help explain the trends seen in this profile?

- [ ] at higher pH, the H^{+} concentration is higher, speeding up acid-catalysed hydrolysis
- [ ] at higher pH, the OH^{-} concentration is higher, speeding up base-catalysed hydrolysis
- [ ] at lower pH, the H^{+} concentration is higher, speeding up acid-catalysed hydrolysis
- [ ] at lower pH the OH^{-} concentration is higher, speeding up base-catalysed hydrolysis

Part C $\mathrm{pH}\ 5.5$

At $\mathrm{pH}\ 5.5$, the rate for the acid hydrolysis reaction is the same as the rate for the alkaline hydrolysis reaction. What are the concentrations of H^+ and OH^- at this pH?

Give your answers to 2 sf.

Concentration of H^+:

Concentration of OH^-:

Part D Rate constant comparison

Which of the following statements about the rate constants for the two hydrolysis processes is/are correct?

- [ ] The rate constants for the acid and alkaline hydrolysis are equal, as the rate for both processes can be made equal under certain conditions.
- [ ] The rate constant for the acid hydrolysis is higher than the rate constant for the alkaline hydrolysis, as the rate for both processes is equal when the H^+ concentration is higher than the OH^- concentration.
- [ ] The rate constant for the alkaline hydrolysis is higher than the rate constant for the acid hydrolysis, as the rate for both processes is equal when the H^+ concentration is higher than the OH^- concentration.
- [ ] The rate constant for the acid hydrolysis is higher than the rate constant for the alkaline hydrolysis, as the acid hydrolysis dominates at neutral pH when the H^+ and OH^- concentrations are equal.
- [ ] The rate constant for the alkaline hydrolysis is higher than the rate constant for the acid hydrolysis, as the alkaline hydrolysis dominates at neutral pH when the H^+ and OH^- concentrations are equal.

Adapted with permission from OCSEB, STEP Chemistry, June 1991, Question 1.

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Cobalt Complexes Equilibrium

A Level

This question is about the following equilibrium:

$$\underset{\text{blue}}{\mathrm{CoCl_4}^{2-}}\,(\mathrm{aq}) + 6\,\mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \underset{\text{pink}}{[\mathrm{Co(H_2O)_6}]^{2+}}\,(\mathrm{aq}) + 4\,\mathrm{Cl^-}\,(\mathrm{aq})$$

Part A Temperature dependence

Two students decided to investigate this equilibrium. They are supplied with the equilibrium mixture at room temperature.

• One student heats $20\,\mathrm{cm}^3$ of the mixture to $50\,^\circ\mathrm{C}$.

• The other student heats $20\,\mathrm{cm}^3$ of the mixture to $90\,^\circ\mathrm{C}$.

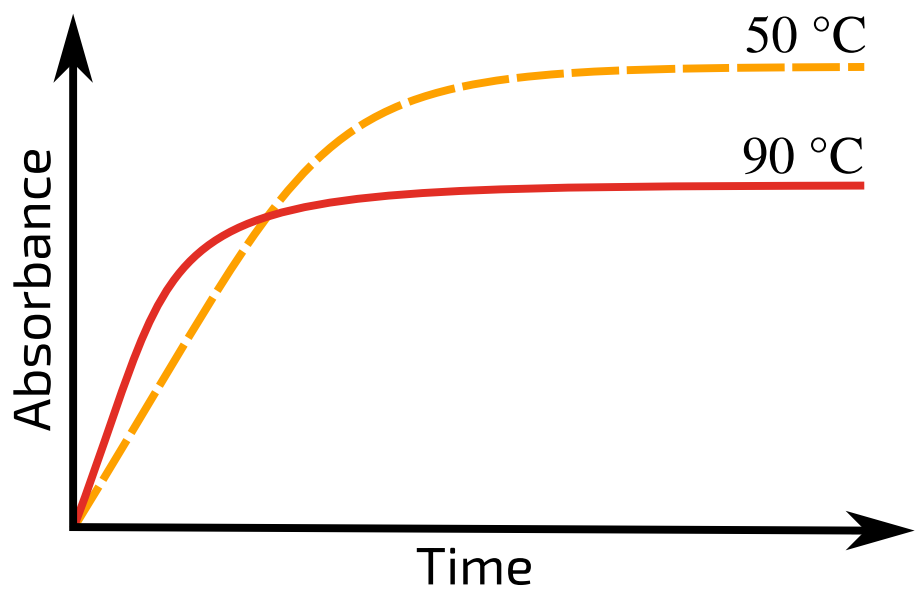
The students use colorimetry to observe how the colour of the equilibrium mixture changes over time.

• The colorimeter is set up so that the greater the absorbance, the greater the concentration of $[\mathrm{Co(H_2O)_6}]^{2+}$.

• The initial absorbance is set to zero.

• The absorbance is recorded every 30 seconds.

The students plot the graph below from the results of the experiment.



At the [ ] temperature, particles have more kinetic energy: they move faster and have [ ] collisions. Each collision is also [ ] likely to exceed the activation energy and therefore be successful, leading to a [ ] rate of reaction. This explains the steeper initial gradient.

However, at this temperature, the plateau occurs at a [ ] value of absorbance, indicating the equilibrium concentration of $[\mathrm{Co(H_2O)_6}]^{2+}$ is [ ]. This means the enthalpy of the products is [ ] than the enthalpy of the reactants.

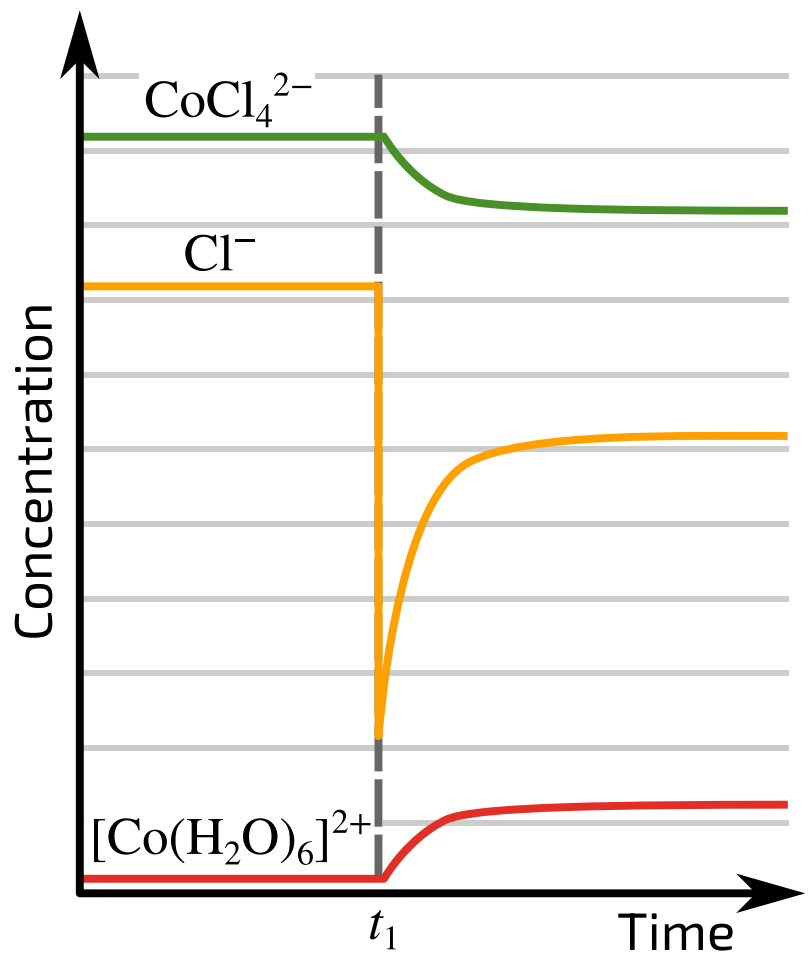
Items:

higher **lower** **less** **more** **fewer**

Part B Silver nitrate

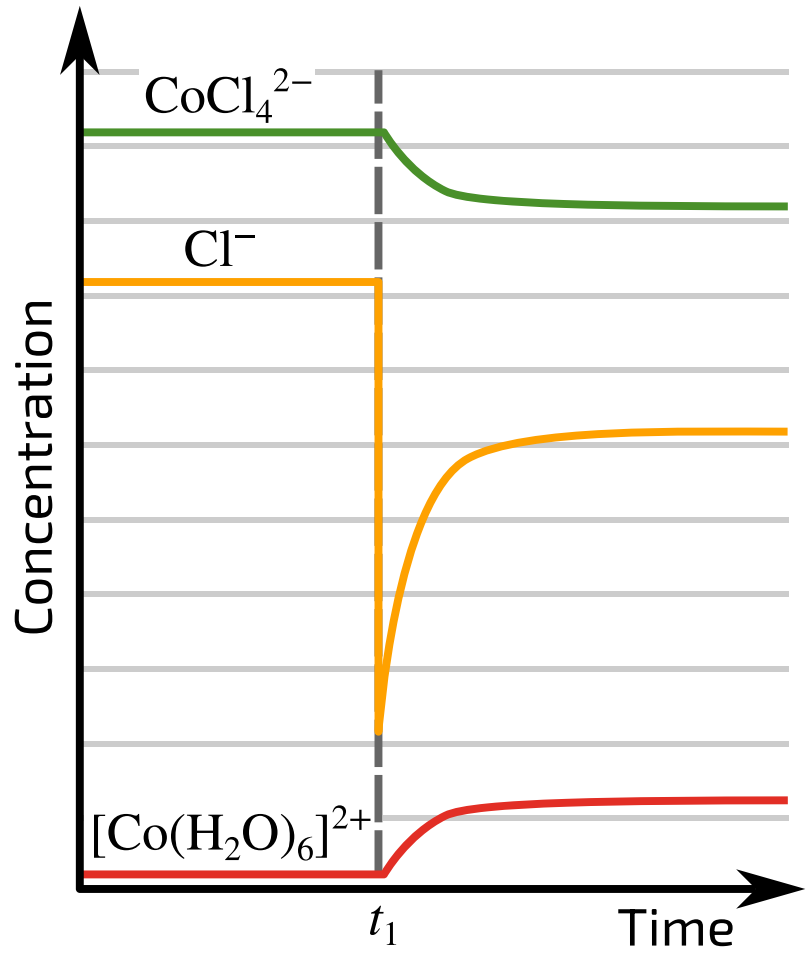
The students investigate how addition of aqueous silver nitrate, $\mathrm{AgNO_3\,(aq)}$, affects the equilibrium position. The graph below shows the changes in the equilibrium concentrations of $\mathrm{CoCl_4^{2-}}$, $\mathrm{Cl^-}$ and $\mathrm{[Co(H_2O)_6]^{2+}}$ after addition of the $\mathrm{AgNO_3\,(aq)}$.

The $\mathrm{AgNO_3\,(aq)}$ is added at time = t_1.



Write an ionic equation, including state symbols, which explains the sharp drop in the $\mathrm{Cl^-}$ concentration at time = t_1.

Part C Reequilibration



As a result of adding silver nitrate, the equilibrium shifts [ ]. The concentration of $[Co(H_2O)_6]^{2+}(aq)$ [ ] after time = t_1, while the concentration of $[CoCl_4]^{2-}(aq)$ [ ] by [ ] as much. The concentration of $Cl^-(aq)$ [ ] by [ ] as much.

Items:

decreases **equally** **increases** **six times** **left** **five times** **thrice** **four times** **twice** **right**

Part D Valence electrons

The colours of the two cobalt complexes are due to transitions of valence electrons between different energy levels.

How many valence electrons does a Co^{2+} ion have?

Part E Geometries

This ligand substitution reaction is accompanied by a change in geometry of the transition metal complex. Describe this change in the format "X to Y" (for example, "linear to trigonal planar").

Parts A-C adapted with permission from OCR, A Level Chemistry A, June 2022, H432/03, Question 4;
Parts D-E created for isaacphysics.org by Andrea Chlebikova

Gameboard:
STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

A Bidentate Ligand

A Level

A bidentate ligand has two lone pairs of electrons that it can donate to a transition metal ion, to form two coordinate bonds.

Part A Synthesis

A bidentate ligand can be produced by reacting 1,2-dichloroethane with two equivalents of ammonia.

Use the structure editor to draw the bidentate ligand that forms in this reaction.

Give your answer as a SMILES string.

In the editor, after drawing your structure, click on the round, yellow smiley face to generate a SMILES string. Copy the SMILES string and paste it in the answer box.

Using the structure editor

Part B Cobalt complex

The Co^{3+} ion can form a complex by associating with three molecules of this bidentate ligand per metal ion. How many different isomers of this complex exist?

Part C Complex cobalt complex

The Co^{3+} ion can also form a complex by associating with two chloride ions and two molecules of the bidentate ligand per metal ion. How many different isomers of this complex exist?

Part D EDTA

The bidentate ligand can be used to synthesise EDTA, by replacing each hydrogen bonded to a nitrogen with a side-chain featuring a carboxylate group. Each carboxylate group can donate a lone pair each. How would you describe this ligand, in reference to the number of dative bonds it forms?

Created for isaacphysics.org by Andrea Chlebikova

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Al and Fe

A Level
C C C

Aluminium, Al, and iron, Fe, are both metallic elements. However, their compounds show significant differences in their properties. For example, aluminium compounds are usually colourless and they contain the metal in only one oxidation state. In contrast, most iron compounds are coloured and the metal can be present in a variety of oxidation states.

Part A Al configuration

What is the ground-state electron configuration of Al?

Items:

[Ne] [Ar] [Kr] [Xe] 3s 4s 3p 3d 4p 1 2 3 4 5 6

Part B Fe configuration

What is the ground-state electron configuration of Fe?

Items:

[Ne] [Ar] [Kr] [Xe] 3s 4s 3p 3d 4p 1 2 3 4 5 6

Part C Al oxidation state

What is the only non-zero oxidation state observed for aluminium?

Part D Oxidation states of Fe

What are the two commonly found non-zero oxidation states for Fe?

- [ ] +1
- [ ] +2
- [ ] +3
- [ ] +4
- [ ] +6
- [ ] +7
- [ ] +8

Part E Maximum oxidation state of Fe

In theory, what is the highest oxidation state possible for Fe?

Part F Thiocyanate ion

A common test for the presence of Fe ions is the addition of thiocyanate ions, $(\mathrm{SCN})^-$. The result is a blood-red colour, caused by the formation of the complex ion $[\mathrm{Fe(SCN)}]^{2+}$.

Using the structure editor, draw a possible structure for the thiocyanate ion. Give your answer as a SMILES string copied from the editor (click the smiley face in the top left of the editor to generate this).

Adapted with permission from OCSEB, STEP Chemistry, June 1995, Question 6.

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Palladium(II) salts

A Level

C C C

Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $\mathrm{PdN_2H_6Cl_2}$. Two of these, **A** and **B**, are neutral complexes, with $M_r = 211$. **A** has a dipole moment whereas **B** has none. The third compound, **C**, is ionic with $M_r = 422$ and contains palladium in both its cation and anion.

Part A Compounds A and B

What is the formula of compounds **A** and **B**? Give your answer starting with the metal ion followed by any ligands.

Part B A and B isomerism

What kind of isomerism is present between compounds **A** and **B**?

Part C Compound C cation

Give the formula and charge of cation of compound **C** in the format $[\mathrm{Pd}\cdots]^{n+}$.

Part D Compound C anion

Give the formula and charge of anion of compound **C** in the format $[\mathrm{Pd}\cdots]^{n-}$.

Adapted with permission from UCLES A-Level Chemistry June 1993, Paper 2, Question 1.

Gameboard:

STEM SMART Chemistry Week 45

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.

Oxidation of Vanadium

A Level

C C C

A $0.0100\,\mathrm{mol}$ sample of an oxochloride of vanadium, VOCl_x, required $20.0\,\mathrm{cm}^3$ of $0.100\,\mathrm{mol\,dm}^{-3}$ acidified potassium manganate(VII) for oxidation of the vanadium.

Part A Moles of electrons

How many moles of electrons were removed by the $\mathrm{MnO_4}^-$ ions?

Part B Change in oxidation state

By how much did the oxidation state of vanadium change? Enter, for example, -2 if it went down by two, +2 if it went up by two, 0 if it did not change.

Part C Value of x

What is the value of x in the formula VOCl_x?

Adapted with permission from UCLES, A-Level Chemistry, June 1993, Paper 2, Question 2.

All materials on this site are licensed under the **Creative Commons license**, unless stated otherwise.