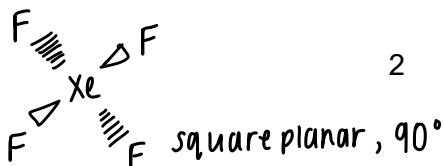


A- level
Chemistry
Physical Chemistry

Total number of marks: 55

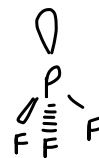


trigonal pyramidal, 107°

07

The melting point of XeF_4 is higher than the melting point of PF_3

Explain why the melting points of these two compounds are different.



In your answer you should give the shape of each molecule, explain why each molecule has that shape and how the shape influences the forces that affect the melting point.

[6 marks]

XeF_4 has a square planar shape, with 90° bond angles around the central Xenon atom and

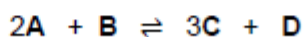
2 lone pairs of electrons around Xenon. Xenon has 8 electrons in its outer shell and each Fluorine atom has 7 outer electrons, therefore forms one covalent bond with Xe, giving a total of 4 bonding pairs of electrons and 2 lone pairs. Lone pairs repel more than bonding pairs and so repel to be as far apart as possible, giving a square planar shape.

PF_3 has a trigonal pyramidal shape with 107° bond angles and one lone pair of electrons. Phosphorus has 5 electrons in its outer shell and shares one electron pair with each fluorine atom, therefore giving 3 bonding pairs and one lone pair. Since lone pair - bond pair repulsion is greater than bond pair - bond pair repulsion, the bonding pairs are pushed together and the bond angle decreases from 109.5° to 107° .

XeF_4 has a higher ^{melting point} than PF_3 because it is a larger molecule and has stronger intermolecular forces. XeF_4 also has a square planar shape so it can be packed more tightly together. Hence, more energy is required to break the intermolecular forces in XeF_4 .

0 4

Compounds **A** and **B** react together to form an equilibrium mixture containing compounds **C** and **D** according to the equation



0 4 . 1

A beaker contained 40 cm^3 of a 0.16 mol dm^{-3} aqueous solution of **A**.
 $9.5 \times 10^{-3} \text{ mol}$ of **B** and $2.8 \times 10^{-2} \text{ mol}$ of **C** were added to the beaker and the mixture was left to reach equilibrium.

The equilibrium mixture formed contained $3.9 \times 10^{-3} \text{ mol}$ of **A**.

Calculate the amounts, in moles, of **B**, **C** and **D** in the equilibrium mixture.

[5 marks]

moles of A :
 0.04×0.16
 $= 0.0064$

| | $2\text{A} + \text{B} \rightleftharpoons$ | | 3C | + | D |
|-----------|---|----------|-------------|---|------------|
| initial n | 0.0064 | 0.0095 | 0.028 | | 0 |
| change | -0.0025 | -0.00125 | +0.00375 | + | 0.00125 |
| equili. n | 0.0039 | 0.00825 | 0.03175 | | 0.00125 |

Amount of **B** 0.00825 mol

Amount of **C** 0.03175 mol

Amount of **D** 0.00125 mol

0 4 . 2

Give the expression for the equilibrium constant (K_c) for this equilibrium and its units.

[2 marks]

$$K_c = \frac{[\text{C}]^3 [\text{D}]}{[\text{A}]^2 [\text{B}]}$$

$$\text{units} = \frac{(\text{mol dm}^{-3})^3 \times \text{mol dm}^{-3}}{(\text{mol dm}^{-3})^2 \times \text{mol dm}^{-3}}$$

$$= \text{mol dm}^{-3}$$

Units mol dm⁻³

0 4 . 3

A different equilibrium mixture of these four compounds, at a different temperature, contained 0.21 mol of **B**, 1.05 mol of **C** and 0.076 mol of **D** in a total volume of $5.00 \times 10^2 \text{ cm}^3$ of solution.

At this temperature the numerical value of K_c was 116

Calculate the concentration of **A**, in mol dm^{-3} , in this equilibrium mixture.
Give your answer to the appropriate number of significant figures.

[3 marks]

$$116 = \frac{\left(\frac{1.05}{0.5}\right)^3 \left(\frac{0.076}{0.5}\right)}{[A]^2 \left(\frac{0.21}{0.5}\right)}$$

$$\Rightarrow [A] = \sqrt{\frac{9.261 \times 0.152}{116 \times 0.42}}$$

$$\Rightarrow [A] = 0.16997\dots$$

Concentration of **A** 0.17 mol dm^{-3}

0 1

This question is about lattice enthalpies.

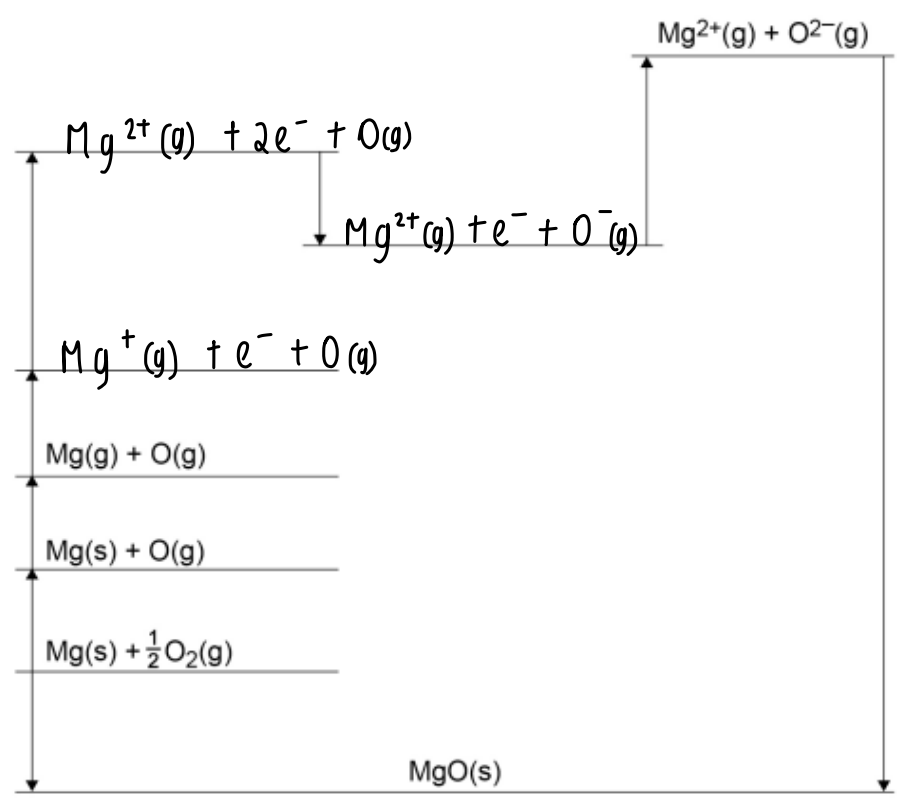
0 1 . 1

Figure 1 shows a Born–Haber cycle for the formation of magnesium oxide.

Complete Figure 1 by writing the missing symbols on the appropriate energy levels.

[3 marks]

Figure 1



0 1 . 2 Table 1 contains some thermodynamic data.

Table 1

| | Enthalpy change / kJ mol^{-1} |
|---|--|
| Enthalpy of formation for magnesium oxide | -602 |
| Enthalpy of atomisation for magnesium | +150 |
| First ionisation energy for magnesium | +736 |
| Second ionisation energy for magnesium | +1450 |
| Bond dissociation enthalpy for oxygen | +496 |
| First electron affinity for oxygen | -142 |
| Second electron affinity for oxygen | +844 |

Calculate a value for the enthalpy of lattice formation for magnesium oxide.

[3 marks]

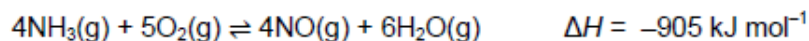
$$150 + (496 \div 2) + 736 + 1450 + 602 - 142 + 844 + x = 0$$

$$\Rightarrow x = -3888 \text{ kJ mol}^{-1}$$

Enthalpy of lattice formation -3888 kJ mol^{-1}

0 3

The equation for the reaction between ammonia and oxygen is shown.

Some standard entropies are given in **Table 3**.**Table 3**

| Gas | $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ |
|--------------------------------|---|
| $\text{NH}_3(\text{g})$ | 193 |
| $\text{O}_2(\text{g})$ | 205 |
| $\text{NO}(\text{g})$ | 211 |
| $\text{H}_2\text{O}(\text{g})$ | 189 |

0 3 . 1

Calculate the entropy change for the reaction between ammonia and oxygen.

[2 marks]

$$\Delta S = [(4 \times 211) + (6 \times 189)] - [(4 \times 193) + (5 \times 205)]$$

$$\Delta S = 181 \text{ J K}^{-1} \text{ mol}^{-1}$$

Entropy change 181 $\text{J K}^{-1} \text{ mol}^{-1}$

0 3 . 2

Calculate a value for the Gibbs free-energy change (ΔG), in kJ mol^{-1} , for the reaction between ammonia and oxygen at $600\text{ }^\circ\text{C} \rightarrow 873\text{ K}$

(If you were unable to obtain an answer to Question 03.1, you should assume that the entropy change is $211\text{ J K}^{-1}\text{ mol}^{-1}$. This is **not** the correct answer.)

[2 marks]

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= -905 - 873(0.181)\end{aligned}$$

$$\Delta G = -1063.013$$

$$\Delta G \underline{-1063} \text{ kJ mol}^{-1}$$

0 3 . 3

The reaction between ammonia and oxygen was carried out at a higher temperature.

Explain how this change affects the value of ΔG for the reaction.

[2 marks]

ΔG would become more negative so the reaction would be more feasible.

0 1

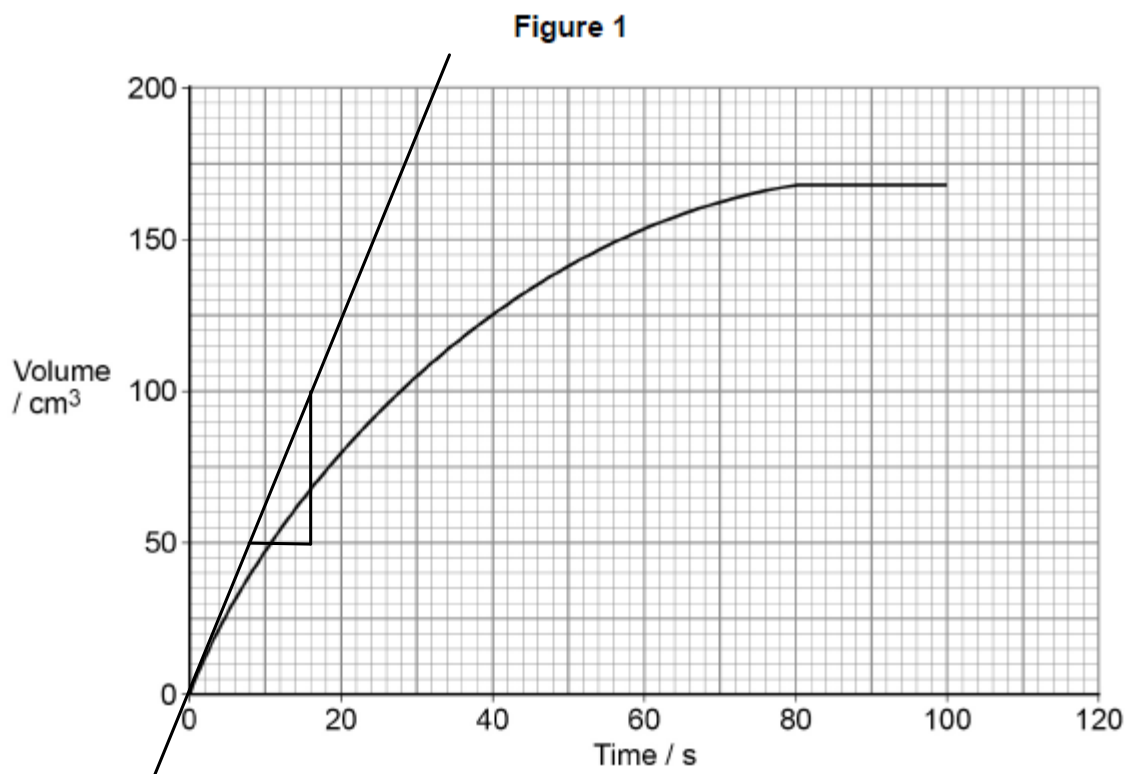
This question is about rates of reaction.

Phosphinate ions (H_2PO_2^-) react with hydroxide ions to produce hydrogen gas as shown.



A student completed an experiment to determine the initial rate of this reaction. The student used a solution containing phosphinate ions and measured the volume of hydrogen gas collected every 20 seconds at a constant temperature.

Figure 1 shows a graph of the student's results.



0 1 . 1

Use the graph in **Figure 1** to determine the initial rate of reaction for this experiment. State its units. Show your working on the graph.

[3 marks]

$$\frac{100 - 50}{16 - 8} = \frac{50}{8} = 6.25 \text{ cm}^3 \text{ s}^{-1}$$

Rate 6.25 Units $\text{cm}^3 \text{ s}^{-1}$

0 1 . 2

Another student reacted different initial concentrations of phosphinate ions with an excess of hydroxide ions. The student measured the time (t) taken to collect 15 cm^3 of hydrogen gas. Each experiment was carried out at the same temperature. **Table 1** shows the results.

Table 1

| Initial $[\text{H}_2\text{PO}_2^-] / \text{mol dm}^{-3}$ | t / s |
|--|----------------|
| 0.25 | 64 |
| 0.35 | 32 |
| 0.50 | 16 |
| 1.00 | 4 |

State the relationship between the initial concentration of phosphinate and time (t).

Deduce the order of the reaction with respect to phosphinate.

[2 marks]

Relationship inverse

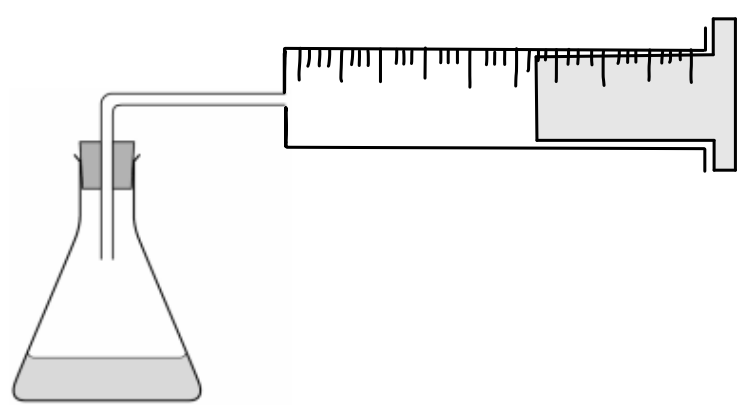
Order 2

0 1 . 3

Complete the diagram in **Figure 2** to show how the hydrogen gas could be collected and measured in the experiments in Questions **01.1** and **01.2**.

[1 mark]

Figure 2



The rate equation for a different reaction is

$$\text{rate} = k [\text{L}] [\text{M}]^2$$

0 1 . 4

Deduce the overall effect on the rate of reaction when the concentrations of both **L** and **M** are halved.

[1 mark]

the rate of reaction would decrease by 0.125 x

0 6

Standard electrode potentials are measured by comparison with the standard hydrogen electrode.

0 6 . 1

State the substances and conditions needed in a standard hydrogen electrode.

[3 marks]

platinum (inert) electrode, HCl at 1 mol dm^{-3} ,
 H_2 gas at 1 atm pressure and temperature
of 25°C (298 K)

0 6 . 4 Table 2 shows some electrode potential data.

Table 2

| Electrode reaction | E^\ominus / V |
|---|-----------------|
| $2H^+(aq) + 2e^- \rightarrow H_2(g)$ | 0.00 |
| $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ | +0.34 |
| $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ | +0.96 |

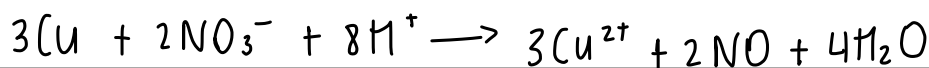
Use the data in Table 2 to explain why copper does **not** react with most acids but does react with nitric acid.

Give an equation for the reaction between copper and nitric acid.

[3 marks]

Explanation most acids have a more negative E^\ominus than copper so are not strong enough oxidising agents to oxidise copper, however the E^\ominus of NO_3^- is greater than the E^\ominus of Cu so NO_3^- oxidises Cu to Cu^{2+} because it is a stronger oxidising agent than Cu.

Equation



0 2

This question is about sulfuric acid and its salts.

0 2 . 2

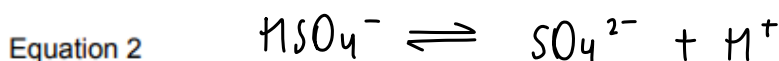
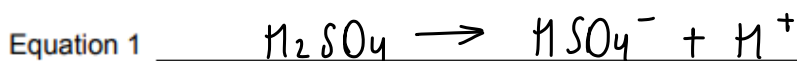
In aqueous solution, sulfuric acid acts as a strong acid. The H_2SO_4 dissociates to form HSO_4^- ions and H^+ ions.

The HSO_4^- ions act as a weak acid and dissociate to form SO_4^{2-} ions and H^+ ions.

Give an equation to show each stage in the dissociation of sulfuric acid in aqueous solution.

Include appropriate arrows in your equations.

[2 marks]



0 2 . 4

A solution that contains 605 mg of NaHSO_4 in 100 cm^3 of solution has a pH of 1.72

Calculate the value of K_a for the hydrogensulfate ion (HSO_4^-) that is behaving as a weak acid.

Give your answer to three significant figures.

State the units of K_a

$$K_a = \frac{[\text{HSO}_4^-][\text{H}^+]}{[\text{NaHSO}_4]}$$

$$[\text{HSO}_4^-] = [\text{H}^+]$$

$$\therefore K_a = \frac{(0.0190546)^2}{0.05037469}$$

$$K_a = 7.21 \times 10^{-3}$$

$$[\text{NaHSO}_4] \quad [6 \text{ marks}]$$

$$\text{moles} = \frac{0.605}{120.1} = 0.0050374$$

$$\text{concentration of NaHSO}_4 = \frac{0.0050374}{0.1}$$

$$= 0.05037469$$

$$[\text{H}^+] = 10^{-1.72} = 0.0190546$$

$$K_a \quad \underline{7.21 \times 10^{-3}}$$

$$\text{Units} \quad \underline{\text{mol dm}^{-3}}$$

0 8

Which has a bond angle of 109.5° ?

[1 mark]

A C (diamond)



B C (graphite)



C NH_2^-



D NH_3



1 3

Which statement about pH is correct?

[1 mark]

- A The pH of a weak base is independent of temperature.
- B At temperatures above 298 K, the pH of pure water is less than 7.
- C The pH of 2.0 mol dm⁻³ nitric acid is approximately 0.30
- D The pH of 0.10 mol dm⁻³ sulfuric acid is greater than that of 0.10 mol dm⁻³ hydrochloric acid.

3 2

Which is the concentration of NaOH(aq), in mol dm⁻³, that has pH = 14.30?

$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 25 °C

[1 mark]

- A -1.16 $[H^+] = 10^{-14.3} = 5.01 \times 10^{-15}$
- B 5.01×10^{-15} $1 \times 10^{-14} = [OH^-](5.01 \times 10^{-15})$
- C 2.00×10^{14} $\therefore [OH^-] = 1.99526 \dots$
- D 2.00

1 1

In which conversion is the metal reduced?

[1 mark]

- A $\overset{+6}{Cr_2O_7^{2-}} \rightarrow \overset{+6}{CrO_4^{2-}}$
- B $\overset{+6}{MnO_4^{2-}} \rightarrow \overset{+7}{MnO_4^-}$
- C $\overset{+4}{TiO_2} \rightarrow \overset{+4}{TiO_3^{2-}}$
- D $\overset{+5}{VO_3^-} \rightarrow \overset{+4}{VO^{2+}}$

3 3

What are the units of the rate constant for a third order reaction?

[1 mark]

- A mol dm⁻³ s⁻¹ $\text{rate} = k [A]^3$
- B mol⁻¹ dm³ s⁻¹ $k = \frac{\text{mol dm}^{-3}}{\text{mol}^3 \text{ dm}^{-9}}$
- C mol² dm⁻⁶ s⁻¹
- D mol⁻² dm⁶ s⁻¹

3 4

What is the pH of $0.015 \text{ mol dm}^{-3}$ sulfuric acid?

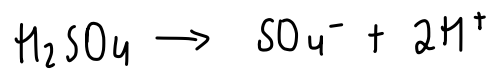
[1 mark]

A -1.82

B -1.52

C 1.52

D 1.82



$$[\text{H}_2\text{SO}_4] = 2[\text{H}^+]$$

$$0.015 \times 2 = 0.03$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] \\ &= -\log(0.03) \end{aligned}$$