NATIONAL
Junior College

Physical Chemistry Revision Part 2

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1) Chemical Equilibrium
MCQ

1 Nitrogen dioxide decomposes on heating according to the following equation.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 4 mol of nitrogen dioxide were put in a 1 dm^3 container and heated, the equilibrium mixture contained 0.8 mol of oxygen.

What is the equilibrium constant, K_c, at the temperature of the experiment?

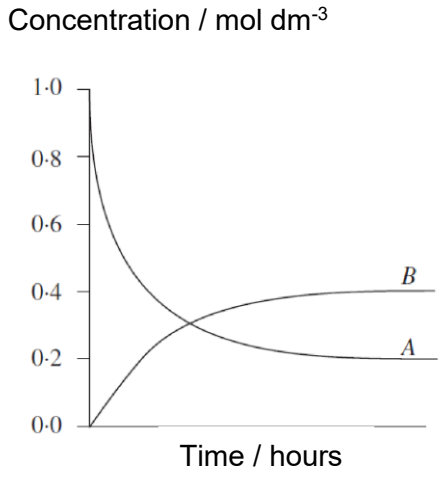
A $\dfrac{0.8 \times 0.8^2}{2.4^2}$ **B** $\dfrac{0.8 \times 1.6^2}{2.4^2}$

C $\dfrac{0.8 \times 0.8^2}{4^2}$ **D** $\dfrac{0.8 \times 1.6^2}{4^2}$

2 If compound **A** is heated, it decomposes according to the equation:

$$2\mathbf{A}(g) \rightleftharpoons \mathbf{B}(g) + \mathbf{C}(g)$$

The following diagram shows the progress of the reaction.



Determine the value of equilibrium constant K_c.

A 0.8 **B** 2.0 **C** 4.0 **D** 10.0

3 The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen to form sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

When 0.50 mol of SO_2 and 1.00 mol of O_2 were reacted together in a container of volume 0.5 dm^3, 0.30 mol of SO_3 was present in the equilibrium mixture.

What is the numerical value of the equilibrium constant, K_c, for the equilibrium reaction below?

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

A 0.66 **B** 1.15 **C** 1.32 **D** 1.63

4 Consider the following equilibrium:

$$2Q_2(g) + R_2(g) \rightleftharpoons 2Q_2R(g)$$

When Q_2 is allowed to react with R_2 in a molar ratio of 2:1 at a total initial pressure of 3 atm, 20% of the equilibrium mixture is found to be Q_2R.

What is the equilibrium constant, K_p, of this reaction?

A 0.0174 atm^{-1}

B 0.0781 atm^{-1}

C 0.194 atm^{-1}

D 0.232 atm^{-1}

5 The contact process is an important industrial reaction which produces sulfuric acid. One of the steps of the process involves the addition of excess oxygen to sulfur dioxide to produce sulfur trioxide gas in an equilibrium reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$SO_2(g)$ and $O_2(g)$ were mixed in a 1:2 ratio and the mixture was kept at a constant pressure of 5 atm. At equilibrium, it was found that 30% of the sulfur dioxide was consumed.

What is the numerical value of K_p of this reaction?

A 0.0566 **B** 0.142

C 1.75 **D** 8.35

6 A 1:3 molar mixture of X_2 and Y_2 is heated at 673 K and 100 atm of constant pressure so that it comes to equilibrium. The equilibrium mixture contains 20 % of XY_3.

$$X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3(g)$$

Using the equation above, what is the numerical value of K_p for the reaction at 673 K?

A 9.26×10^{-5} **B** 2.93×10^{-4}

C 2.50×10^{-4} **D** 5.68×10^{-4}

7 Ammonia decomposes into hydrogen and nitrogen gas at high temperatures.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Ammonia at pressure P was placed in an evacuated reactor which was maintained at constant temperature. At equilibrium, the ratio of nitrogen to ammonia was found to be 1:3.

What is the equilibrium constant, K_p, for the reaction?

A $3P^2$ **B** $75P^2$

C $\frac{P^2}{3}$ **D** $\frac{3P^2}{25}$

8 The following reaction is used industrially to produce a combustible gas from coal.

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$$

A mixture of powdered coal and steam at a pressure of 1 atm was allowed to reach equilibrium at a constant temperature of 500 K. At equilibrium, the total pressure had increased to 1.9 atm.

What is the numerical value of the equilibrium constant, K_p, at 500 K?

A 1.9 **B** 3.24

C 8.1 **D** 81

9 A pure sample of $NH_3(g)$ is introduced into an evacuated vessel of constant volume. This vessel is maintained at constant temperature such that the equilibrium below is established.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

The value of the final pressure is then found to be 40 % greater than if only NH_3 were present. What is the mole fraction of H_2 in the reaction mixture?

A 0.14 **B** 0.29

C 0.43 **D** 0.72

10 Given the following reaction:

$$\mathbf{A}\,(g) + \mathbf{B}\,(g \rightleftharpoons 2\mathbf{C}\,(g) + 2\mathbf{D}\,(g) \qquad K_p = 2.10 \times 10^2\ atm^2$$

An equimolar mixture of **A** and **B** is allowed to reach equilibrium at 700 K. Determine the total pressure at equilibrium if the partial pressure of **C** at equilibrium is found to be 2.00 atm.

A 1.28 atm
B 4 atm
C 4.28 atm
D 4.56 atm

11 Given that the K_p for the following equilibrium is 125 at 65°C,

$$\mathbf{X}(s) + 3\mathbf{Y}(g) \rightleftharpoons 3\mathbf{Z}(g)$$

What is the mole ratio of **Y** : **Z** at equilibrium at 65°C?

A 1 : 1
B 1 : 5
C 25 : 1
D 125 : 1

12 An equilibrium can be represented by the following equation:

$$\mathbf{P}(aq) + \mathbf{Q}(aq) \rightleftharpoons 2\mathbf{R}(aq) + \mathbf{S}(aq)$$

In a certain mixture, the equilibrium concentration of **Q** is 10 mol dm^{-3}.
What will be the new equilibrium concentration of **Q** if 5 mol of pure **Q** is dissolved in the mixture?

A 15 mol dm^{-3}
B between 10 mol dm^{-3} and 15 mol dm^{-3}
C 10 mol dm^{-3}
D between 5 mol dm^{-3} and 10 mol dm^{-3}

13 Ammonia is manufactured industrially by the Haber Process as shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

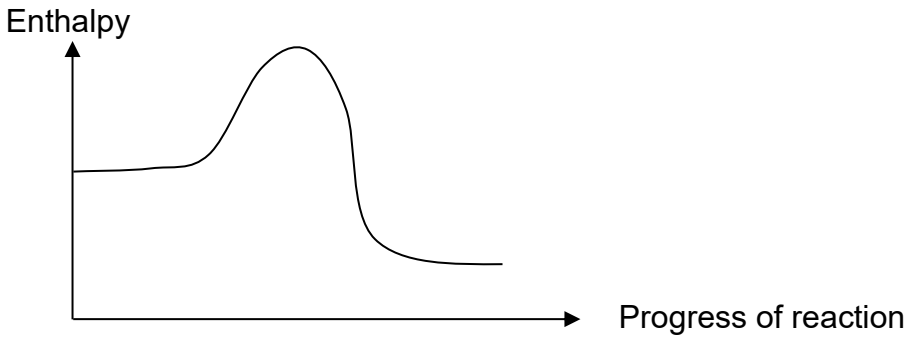
The operating conditions are: 400 to 450 °C; a pressure of 200 atm; an iron catalyst

Which of the following statement(s) is/are **true** about the Haber process for the manufacture of ammonia?

1 At higher temperatures, the production of ammonia becomes thermodynamically less feasible.
2 At higher pressures, the yield goes down but the rate of production of ammonia is faster.
3 The presence of a catalyst shifts the equilibrium position to the right and increases the yield.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

14 The diagram below represents the reaction profile of the monomer-dimer system:



$$2NO_2\,(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} N_2O_4\,(g)$$
brown colourless

Which statement about the equilibrium is correct?

A The equilibrium constant K_c will be larger at higher temperatures.
B k_f increases and k_b decreases when the equilibrium mixture is heated.
C Doubling the total pressure of the system reduces the percentage dissociation to half.
D At higher temperature, the colour intensity of the mixture increases.

15 Ammonia is manufactured in the Haber process.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H^{\ominus} = -92\ kJ\ mol^{-1}$$

Given that K_p for the above reaction is 3.375 at T K, which of the following statements involving the reaction is correct?

1 The partial pressure of H_2 (g) at equilibrium at T K can be expressed as $\frac{2}{3}\left(P_{NH_3}\right)^{2/3}\left(P_{N_2}\right)^{-1/3}$

2 When equilibrium is established, temperature, T K, is given by $T=\frac{\Delta H}{\Delta S}$

3 When pressure is increased, the yield of ammonia and the equilibrium constant increases.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

16 The values of the equilibrium constant, K_p, for the reaction

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

are 0.313 kPa and 115 kPa at 25 °C and 727 °C respectively.
What deduction can be made from the information given above?

A The yield of CO_2 can be increased by adding some Ag_2CO_3 to a system already in equilibrium.
B The activation energy of the reverse reaction is higher than that of the forward reaction.
C Less CO_2 is formed at equilibrium if the reaction is allowed to take place in another container of a smaller volume.
D More CO_2 is formed at equilibrium if a suitable catalyst is used.

17 A system at equilibrium is subjected to the following changes separately:
(i) The pressure is reduced at constant temperature
(ii) The temperature is increased at constant pressure

For which equilibrium will both of these changes result in an increase in the proportion of products?

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = +53$ kJ mol^{-1}
B $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -950$ kJ mol^{-1}
C $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ mol^{-1}
D $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol^{-1}

18 When steam is passed over white hot coke, a mixture of combustible gases is obtained.

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g); \qquad \Delta H = +131 \text{ kJ mol}^{-1}$$

When equilibrium has been established, which of the following correctly describes what would happen if a proposed change is made to this system?

	proposed change	value of K_c	forward rate constant	backward rate constant
1	add catalyst	no change	increase	increase
2	add more C(s)	no change	increase	no change
3	increase temperature	increase	increase	decrease

A **1, 2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

19 Phosphorus pentachloride, PCl_5, is prepared from the chlorination of PCl_3 according to the equation below.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g); \qquad \Delta H = -124 \text{ kJ mol}^{-1}$$

At a constant temperature and a total initial pressure of 2.4 atm, a 1 : 2 mixture of PCl_3 and Cl_2 is allowed to reach equilibrium in a sealed vessel. The percentage yield is found to be 40%.

Which of the following are correct?

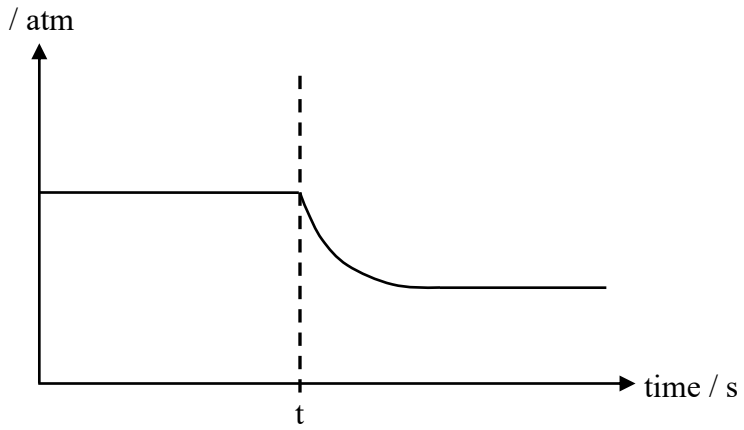
1 PCl_5 has a trigonal bipyramidal shape.
2 The equilibrium constant, K_p, is found to be 0.521 atm^{-1}.
3 When the total volume of the vessel is increased, the percentage yield decreases.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

20 A sealed vessel of fixed volume contains a mixture of CO(g), H_2(g) and CH_3OH(l) at equilibrium.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) \qquad \Delta H < 0$$

At time t, the reaction mixture is subjected to a change. The graph below shows the partial pressure of CO against time.



Which changes, when carried out separately, could have given the graph above?

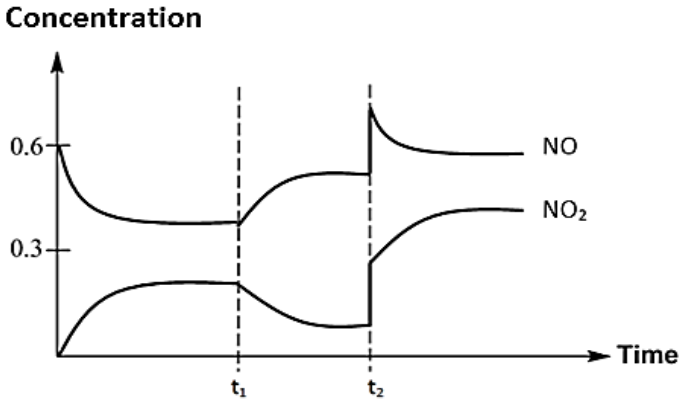
1 addition of H_2(g)
2 removal of some CH_3OH(l)
3 decrease in temperature

A 1, 2 and 3
B 1 and 2 only
C 1 and 3 only
D 3 only

21 At temperature T, 0.60 mol dm^{-3} of NO and 0.30 mol dm^{-3} of O_2 were introduced into a 2 dm^3 vessel and allowed to reach equilibrium.

$$2\ NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2\ (g) \qquad \Delta H < 0$$

The graph below shows the changes in the amounts of NO and NO_2 in the system with time. A change was made to the system at time $\mathbf{t_1}$ and $\mathbf{t_2}$.



What were the changes made at time $\mathbf{t_1}$ and $\mathbf{t_2}$?

	$\mathbf{t_1}$	$\mathbf{t_2}$
A	The temperature was increased	Volume of the system is increased
B	The temperature was decreased	More O_2 was added
C	An inert gas was added at constant volume	More NO_2 was added
D	The temperature was increased	Volume of the system is decreased

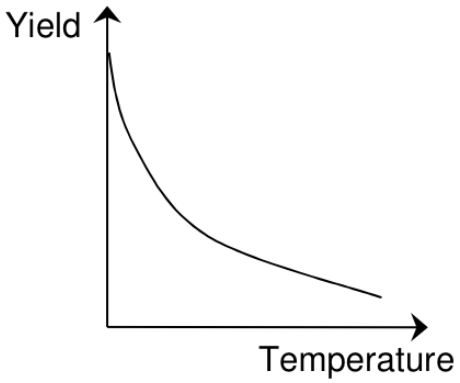
22 *Use of the Data Booklet is relevant to this question.*

Ammonia can be synthesised directly using a mixture of hydrogen gas and nitrogen gas in a reversible reaction as shown:

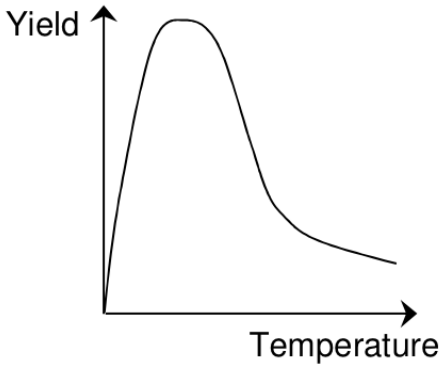
$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

Which one of the following describes the change in yield of ammonia at equilibrium as temperature increases?

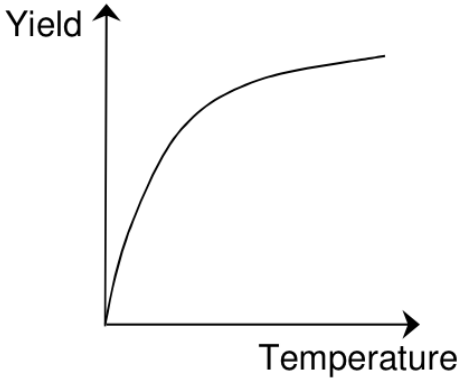
A



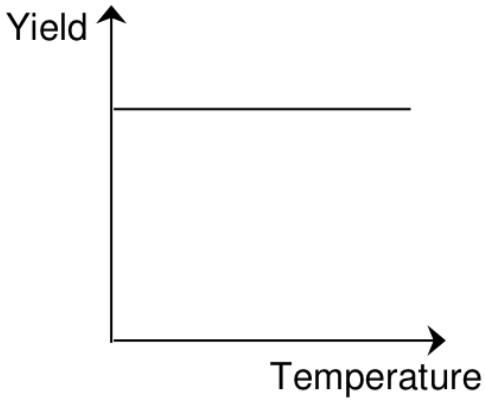
B



C

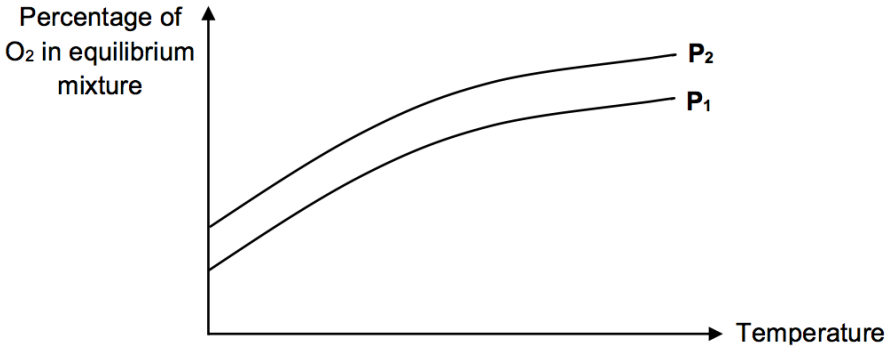


D



23 The graph below shows how the percentage of oxygen gas in the equilibrium mixture shown below varies with temperature at pressures $\mathbf{P_1}$ and $\mathbf{P_2}$.

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$



Which statements about the reaction are correct?

1 The pressure $\mathbf{P_1}$ is larger than $\mathbf{P_2}$.

2 The forward reaction is exothermic.

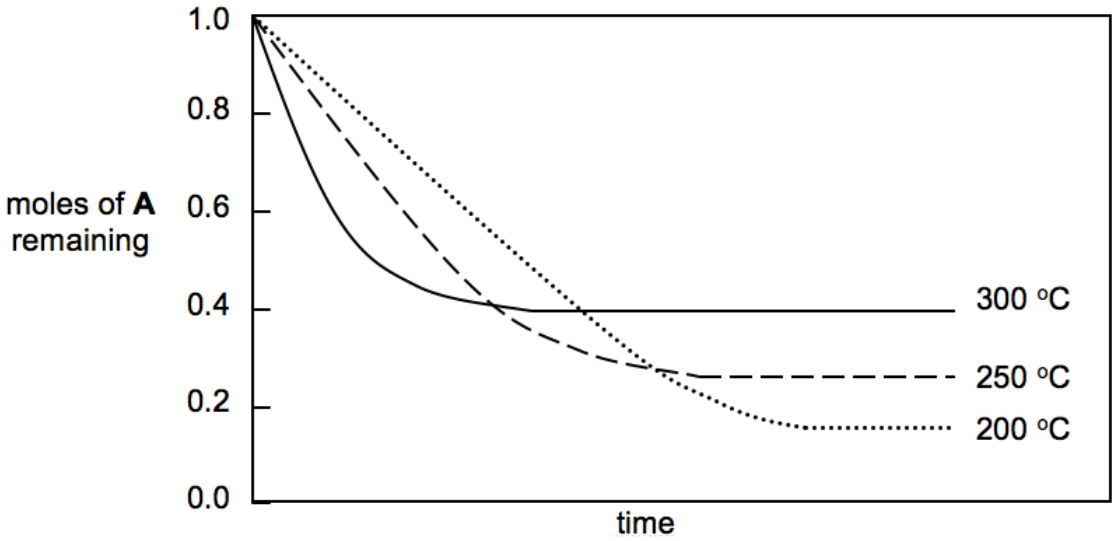
3 Addition of an inert gas into the system will not cause the graph to shift.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

24 Gas **A** decomposes to two other gases, **B** and **C**, according to the following equation:

$$2\mathbf{A}(g) \rightleftharpoons 3\mathbf{B}(g) + \mathbf{C}(g)$$

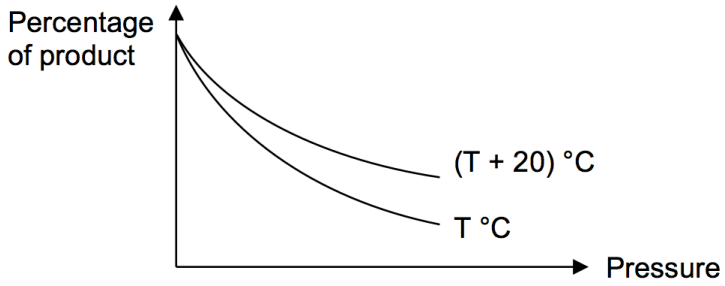
The graph below shows the decomposition of 1.0 mol of pure gas **A** in the presence of a catalyst at various temperatures.



Which one of the following statements about the above system is **incorrect**?

A The decomposition of **A** is endothermic.
B The K_p of the system decreases with increasing temperature.
C The percentage decomposition of **A** is 60 % at 300 °C.
D The system becomes more disordered when it reaches equilibrium state.

25 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.

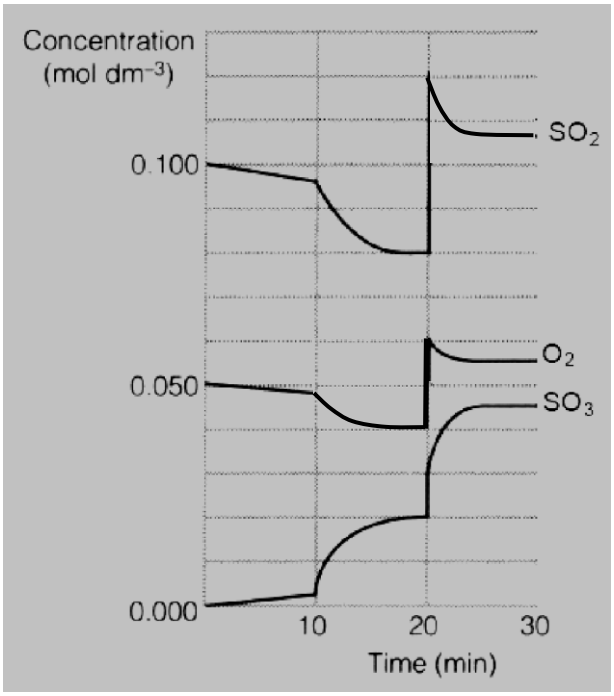


A $4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$ $\Delta H = -1644$ kJ mol^{-1}
B $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -222$ kJ mol^{-1}
C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol^{-1}
D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86$ kJ mol^{-1}

26 During the Contact process, sulfur dioxide is converted to sulfur trioxide as shown by the equation below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \ \Delta H = -197 \text{ kJ mol}^{-1}$$

The graph below shows how the concentration of the three gases changed when a series of changes was made.



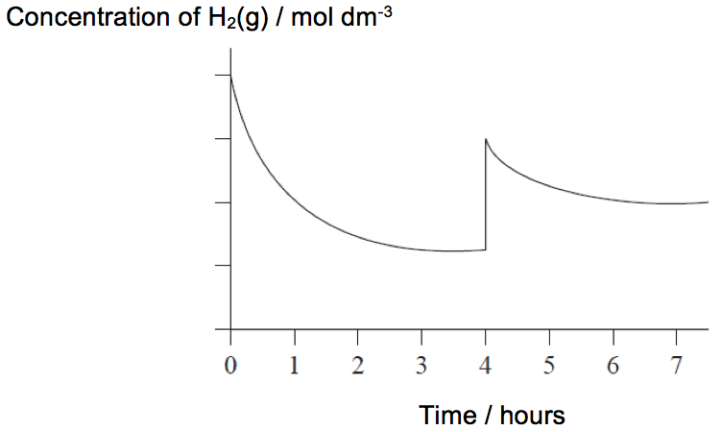
Which conclusion can be drawn from this information?

A At 10 min, some sulfur dioxide gas was removed from the system.
B At 20 min, the numerical value of the equilibrium constant, K_c, was 1.56.
C At 20 min, the pressure of the system was decreased by increasing the volume.
D The temperature of the mixture at 30 min was higher than that at 20 min.

27 The reaction between phosphorus and hydrogen can result in the formation of phosphine as shown:

$$P_4(s) + 6H_2(g) \rightleftharpoons 4PH_3(g)$$

The graph shows the change in concentration of hydrogen for this reaction in which the system was disturbed after four hours.



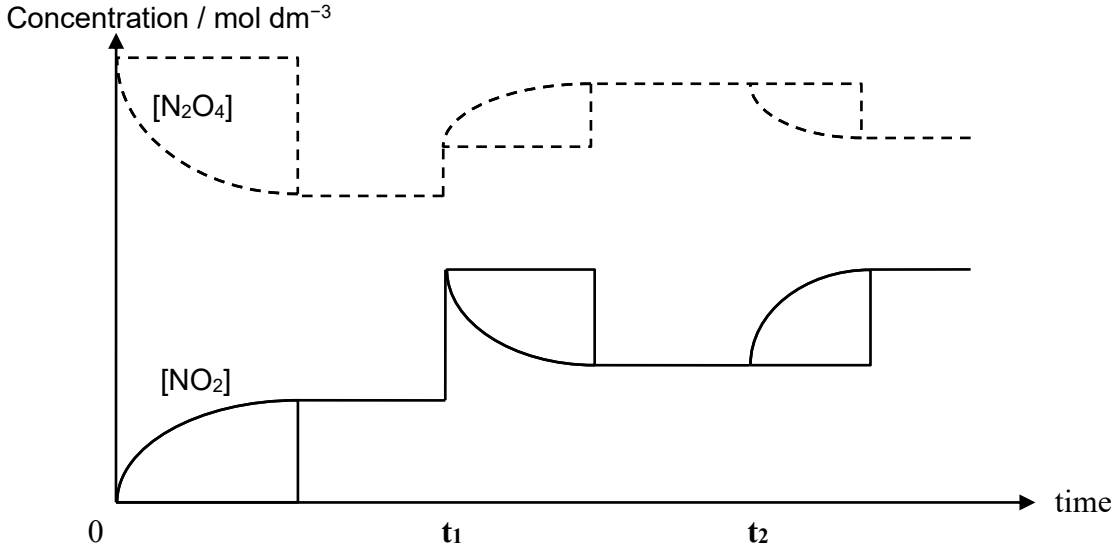
Which could explain the change in the hydrogen concentration at time, t = 4 hours?

A The volume of the reaction vessel was decreased.
B A catalyst was added.
C The pressure on the reaction mixture was decreased.
D More phosphorus was added.

28 Consider the following equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

A certain amount of N_2O_4 was placed in a closed vessel and allowed to reach equilibrium.



Two changes were made to the equilibrium system at $\mathbf{t_1}$ and $\mathbf{t_2}$.

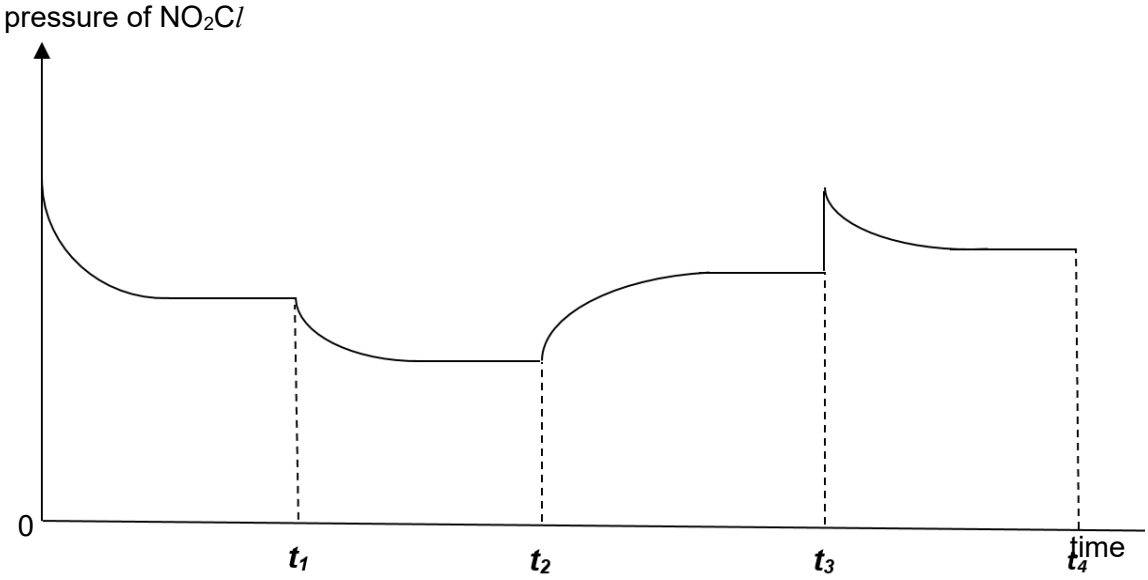
Using the graph above, what are the changes made at $\mathbf{t_1}$ and $\mathbf{t_2}$?

	t_1	t_2
A	[NO_2] increase	[N_2O_4] decrease
B	Pressure increase	[N_2O_4] decrease
C	Volume of vessel decrease	Temperature increase
D	Catalyst added	Temperature increase

29 Nitrosyl chloride, NO*C*l, is a yellow gas that can be formed between nitryl chloride, NO_2C*l*, and nitric oxide, NO, in the following reaction.

$$NO_2C\mathit{l}(g) + NO(g) \rightleftharpoons NOC\mathit{l}(g) + NO_2(g) \qquad \Delta H < 0$$

NO_2C*l* and NO were initially allowed to react in a closed vessel at 800 K and equilibrium was established.
The graph below shows how the pressure of NO_2C*l* varied with time.

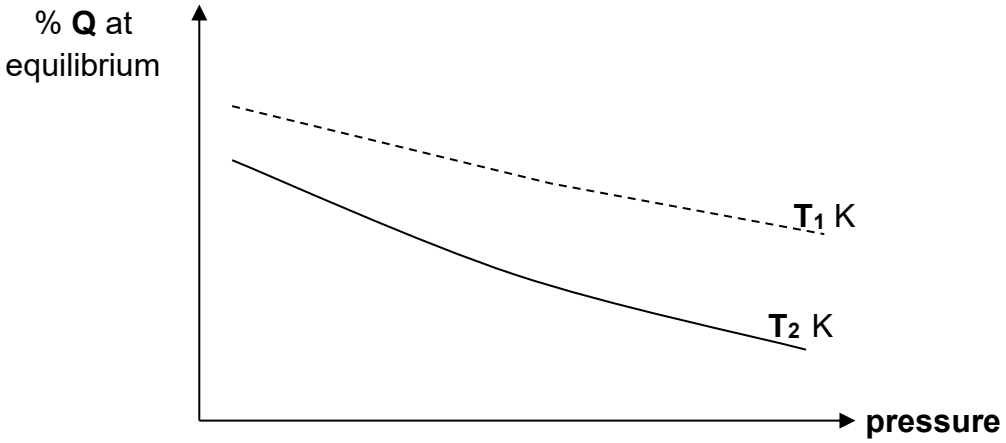


What could be the changes made to the system at t_1, t_2 and t_3?

	t_1	t_2	t_3
A	NO_2C*l* was removed	temperature was increased	NO_2C*l* was added
B	temperature was decreased	NO_2C*l* was added	NO_2 was added
C	NO_2 was removed	temperature was increased	NO_2C*l* was added
D	NO_2C*l* was removed	NO_2C*l* was added	temperature was decreased

30 The graph below shows the variation of the percentage of **Q** present at equilibrium, with temperature and pressure.

$$3O_2\,(g) + 4NH_3\,(g) \rightleftharpoons 2N_2\,(g) + 6H_2O\,(g) \qquad \otimes H = -1248\ kJ\ mol^{-1}$$



Which of the following systems could **Q** represent?

	Q	**Temperature**
A	O_2	$\mathbf{T_1 > T_2}$
B	NH_3	$\mathbf{T_2 > T_1}$
C	N_2	$\mathbf{T_1 > T_2}$
D	H_2O	$\mathbf{T_2 > T_1}$

31 The following process is used to convert methane to hydrogen.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H > 0$$

What will increase the yield of the reaction?

1 Increasing the temperature.

2 Increasing the total pressure by decreasing the total volume at constant temperature.

3 Removing CO and H_2 gas as they are formed but keeping the total volume of the mixture the same.

A 1 **B** 1 and 3 **C** 2 and 3 **D** 3

Structured Questions

1 Hydrazine, N_2H_4, is a colourless flammable liquid with an ammonia-like odour.
It boils at 114 °C, and gaseous hydrazine can decompose to form hydrogen and nitrogen gases.
In a closed reaction vessel of 10 dm^3 maintained at a temperature of 150 °C, gaseous hydrazine decomposes into nitrogen and hydrogen. The system reaches equilibrium with a total pressure of 1 atm. (Take 1 atm = 101 kPa.)

$$N_2H_4(g) \rightleftharpoons N_2(g) + 2H_2(g)$$

The average M_r of the equilibrium gas mixture in the 10 dm^3 vessel is found to be 20.

(a) Calculate the mass of the gaseous mixture inside the reaction vessel at the given temperature and pressure.

The average M_r for this gas mixture can be expressed as
M_r (average) = $\chi_{N_2H_4} \times M_r(N_2H_4) + \chi_{N_2} \times M_r(N_2) + \chi_{H_2} \times M_r(H_2)$
where $\chi_{N_2H_4}$, χ_{N_2} and χ_{H_2} are the mole fractions of N_2H_4, N_2 and H_2 respectively.

(b) **(i)** Show that the degree of dissociation, α, under these conditions has a value of 0.30.

(ii) Using **(i)**, calculate the partial pressure (in atm) of N_2H_4 present at equilibrium.
Hence calculate the value of the equilibrium constant, K_p, of the system.
Show the units of K_p clearly.

2 Water gas is a synthesis gas that consists of carbon monoxide and hydrogen. The gas is made by passing steam over coke:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H > 0$$

When steam was passed over coke at temperatures near 800 °C with a pressure of 8.81 atm and allowed to reach equilibrium in a 1.00 dm^3 vessel, the partial pressure of steam was found to be 2.67 atm.

(i) Write the K_p expression for the reaction. Include units in your answer.

(ii) What is K_p at 800 °C?

(iii) The numerical value of K_p at 25 °C is 1.7×10^{-21}.
Compare the K_p values at 25 °C and 800 °C and comment on their difference in relation to ΔH of the reaction.

3 Iodine is poorly soluble in water. However, it dissolves in solutions containing iodide ions as the soluble I_3^- is formed.

The iodide ions and iodine molecules are in equilibrium with I_3^- (aq) ions as follows:

$$I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)$$

0.080 mol of iodine and 0.058 mol of potassium iodide were dissolved in 500 cm^3 of water until equilibrium is reached.

(i) Write the K_c expression for the equilibrium above, stating its units.

(ii) If 0.0425 mol of iodine is present at equilibrium, find the equilibrium constant of the equilibrium obtained.

4 The simplest chemical reactions are those that occur in the gas phase in a single step, such as the transfer of a chlorine atom from C*l*NO_2 to NO.

$$C\mathit{l}NO_2\,(g) + NO(g) \rightleftharpoons NO_2(g) + C\mathit{l}NO(g)$$

(i) An equimolar mixture of C*l*NO_2(g) and NO(g), at a total initial pressure of 3 atm, was allowed to react in a closed vessel at 1000 K. When equilibrium was attained at the 5th minute, the partial pressure of C*l*NO_2 was found to be 0.57 atm.
Calculate the value for the equilibrium constant, K_p, of this system.

(ii) At the 10th minute, more C*l*NO_2 gas was pumped into the vessel at 1000 K, increasing the partial pressure of C*l*NO_2 to 1 atm.
Suggest how the position of the equilibrium would change.

(iii) Hence illustrate clearly, in the pressure−time graph below, the changes in the partial pressures of C*l*NO_2 and NO_2 when
(I) the above gaseous system first reached equilibrium at the 5th minute,
(II) more C*l*NO_2 gas was added into the vessel at the 10th minute and a new equilibrium was attained at the 15th minute.

5 Ozone, O_3, is unstable with respect to decomposition to diatomic oxygen:

(a)

$$2O_3(g) \rightleftharpoons 3O_2(g) \qquad K_p = 4.0 \times 10^{28}\ \text{Pa at rtp}$$

(i) Write the K_p expression for the decomposition of ozone to diatomic oxygen.

(ii) Ozone occurs quite readily in nature most often as a result of lightning strikes that occur during thunderstorms.
Calculate the partial pressure of oxygen present in 10^6 m^3 of air at rtp after a lightning strike. Assume that the atmosphere of the Earth is 21 % oxygen by volume.

(iii) Hence, calculate the partial pressure of O_3 molecules present at equilibrium.

(b) Nitric oxide, NO, is another molecule responsible for a small portion of the depletion of ozone. It can be produced as shown.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Under standard conditions at 298 K, $K_p = 4 \times 10^{-31}$ but at 2000 K, $K_p = 3 \times 10^{-5}$.

Comment on the change in the value of K_p as the temperature rises and explain its importance to the composition of the exhaust gas from cars.

6 PCl_5 can be produced by reacting PCl_3 with chlorine gas. When a mixture containing 1:1 ratio of PCl_3 and Cl_2 at a total initial pressure of 3.8 atm is allowed to react at 700 K, the partial pressure of PCl_5 formed at equilibrium is found to be 1.68 atm. The standard enthalpy change of this reaction is –418 kJ mol^{-1}.

(i) Calculate the equilibrium partial pressures of PCl_3 and Cl_2.

(ii) Hence, determine the percentage conversion of PCl_3 and the equilibrium constant, K_p.

(iii) Using Le Chatelier's Principle, predict the effect on the yield of PCl_5 when the temperature is increased.

Answers: Chemical Equilibrium MCQ

1	B	2	C	3	B	4	C	5	A
6	A	7	D	8	C	9	C	10	D
11	B	12	B	13	D	14	D	15	B
16	C	17	D	18	D	19	A	20	C
21	D	22	A	23	A	24	A	25	C
26	B	27	A	28	C	29	C	30	D
31	B								

1 Nitrogen dioxide decomposes on heating according to the following equation.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 4 mol of nitrogen dioxide were put in a 1 dm^3 container and heated, the equilibrium mixture contained 0.8 mol of oxygen.

What is the equilibrium constant, K_c, at the temperature of the experiment?

A $\frac{0.8 \times 0.8^2}{2.4^2}$ **B** $\frac{0.8 \times 1.6^2}{2.4^2}$

C $\frac{0.8 \times 0.8^2}{4^2}$ **D** $\frac{0.8 \times 1.6^2}{4^2}$

	$2NO_2$ (g)	$\rightleftharpoons$	2NO (g)	$+O_2$(g)
Initial /mol dm^{-3}	4		0	0
change	– 1.6		+ 1.6	+ 0.8
Eqm /mol dm^{-3}	2.4		1.6	0.8

$$K_c = \frac{0.8 \times 1.6^2}{2.4^2}$$

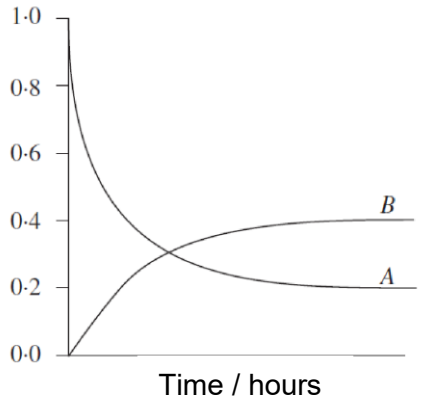
Answer B

2 If compound **A** is heated, it decomposes according to the equation:

$$2\mathbf{A}(g) \rightleftharpoons \mathbf{B}(g) + \mathbf{C}(g)$$

The following diagram shows the progress of the reaction.

Concentration / mol dm^{-3}



Determine the value of equilibrium constant K_c.

A 0.8 **B** 2.0 **C** 4.0 **D** 10.0

	2**A**(g)	⇌	**B**(g) +	**C**(g)
Initial/ mol dm^{-3}	1		0	0
Change/ mol dm^{-3}	−0.8		+0.4	+0.4
Eqm/ mol dm^{-3}	0.2		0.4	0.4

$$K_c = \frac{(\frac{0.4}{V})^2}{(\frac{0.2}{V})^2} = 4.0$$

Answer C

3 The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen to form sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

When 0.50 mol of SO_2 and 1.00 mol of O_2 were reacted together in a container of volume 0.5 dm^3, 0.30 mol of SO_3 was present in the equilibrium mixture.

What is the numerical value of the equilibrium constant, K_c, for the equilibrium reaction below?

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

A 0.66 **B** 1.15 **C** 1.32 **D** 1.63

	2SO_3 (g)	+	O_2 (g)	⇌	2SO_3 (g)
Initial / mol	0.50		1.00		–
Change / mol	– 0.30		– 0.15		+ 0.30
Eqm / mol	0.20		0.85		0.30

$$K = \frac{[SO3]^2}{[SO2]^2[O2]}$$

$$K = \frac{\left(\frac{0.30}{0.5}\right)^2}{\left(\frac{0.20}{0.5}\right)^2 \frac{0.85}{0.5}} = \frac{45}{34}$$

The equilibrium constant expression for the equation $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is written as follows:

$$K_c = \frac{[SO3]}{[SO2][O2]^{0.5}}$$

$$K_c = \sqrt{K} = 1.15$$

Answer B

4 Consider the following equilibrium:

$$2Q_2\,(g) \;+\; R_2\,(g) \rightleftharpoons 2Q_2R(g)$$

When Q_2 is allowed to react with R_2 in a molar ratio of 2:1 at a total initial pressure of 3 atm, 20% of the equilibrium mixture is found to be Q_2R.

What is the equilibrium constant, K_p, of this reaction?

A 0.0174 atm^{-1}

B 0.0781 atm^{-1}

C 0.194 atm^{-1}

D 0.232 atm^{-1}

Since total pressure is 3 atm and the mole ratio between Q_2 and R_2 is 2:1, their respective partial pressure is 2 atm and 1 atm.

$$2Q_2\,(g) \;+\; R_2\,(g) \rightleftharpoons 2Q_2R(g)$$

Initial/am	2	1	0
Change/atm	-2x	-x	+2x
Equilibrium/atm	2 - 2x	1 – x	2x

Total pressure of gas at equilibrium = (2-2x)+(1-x) +2x = 3-x

According to question, 2x/(3-x) = 0.20

x = 0.273 atm

Thus,

partial pressure of Q_2 = 2 – 2(0.273) = 1.454 atm

partial pressure of R_2 = 1– 0.273 = 0.727 atm

partial pressure of Q_2R = 2 x 0.273 = 0.546 atm

$K_p = (0.546)^2 / [(1.454)^2(0.727)] = 0.194\ atm^{-1}$

Answer: C

5 The contact process is an important industrial reaction which produces sulfuric acid. One of the steps of the process involves the addition of excess oxygen to sulfur dioxide to produce sulfur trioxide gas in an equilibrium reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$SO_2(g)$ and $O_2(g)$ were mixed in a 1:2 ratio and the mixture was kept at a constant pressure of 5 atm. At equilibrium, it was found that 30% of the sulfur dioxide was consumed.

What is the numerical value of K_p of this reaction?

A 0.0566 **B** 0.142
C 1.75 **D** 8.35

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

	$2SO_2(g)$	$O_2(g)$	$2SO_3(g)$
Initial/mol	x	2x	0
Change/mol	−0.3x	−0.15x	+0.3x
Eqm/mol	0.7x	1.85x	0.3x

Since pressure is kept constant ie. total pressure at equilibrium is 5 atm.

$5 = 0.7x + 1.85x + 0.3x = 2.85x$

$x = 1.754$

Partial pressure of $SO_2 = 0.7 \times 1.754 = 1.228$ atm

Partial pressure of $O_2 = 1.85 \times 1.754 = 3.245$ atm

Partial pressure of $SO_3 = 0.3 \times 1.754 = 0.5262$ atm

$$K_p = \frac{0.5262^2}{3.2451.228^2} = 0.0566$$

Answer: A

6 A 1:3 molar mixture of X_2 and Y_2 is heated at 673 K and 100 atm of constant pressure so that it comes to equilibrium. The equilibrium mixture contains 20 % of XY_3.

$$X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3(g)$$

Using the equation above, what is the numerical value of K_p for the reaction at 673 K?

A 9.26×10^{-5} **B** 2.93×10^{-4}
C 2.50×10^{-4} **D** 5.68×10^{-4}

$$X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3(g)$$

	$X_2(g)$	$3Y_2(g)$	$2XY_3(g)$
Eqm pressure/atm	100 x0.2 = 20	100 x 0.6 = 60	100 x 0.2 = 20

$$K_p = \frac{20^2}{20(60)} = 9.26 \times 10^{-5}\ \text{atm}^{-2}$$

Answer: A

7 Ammonia decomposes into hydrogen and nitrogen gas at high temperatures.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Ammonia at pressure *P* was placed in an evacuated reactor which was maintained at constant temperature. At equilibrium, the ratio of nitrogen to ammonia was found to be 1:3.

What is the equilibrium constant, K_p, for the reaction?

A $3P^2$ **B** $75P^2$

C $\frac{P^2}{3}$ **D** $\frac{3P^2}{25}$

	$2NH_3(g)$	$\rightleftharpoons N_2(g)$	$+ 3H_2(g)$
Initial pressure	P	0	0
Change	-2x	+x	+3x
Eqm pressure	P-2x =3x	x	3x

At equilibrium, the ratio of nitrogen to ammonia was found to be 1:3.
Since partial pressure of N_2 is x, partial pressure of NH_3 will be 3x.

Total Pressure = 5x $\Rightarrow$ x = $\frac{P}{5}$

Partial pressure of NH_3 = Partial pressure of H_2 = $\frac{3P}{5}$

Partial pressure of N_2 = $\frac{P}{5}$

$K_p = \frac{(\frac{3P}{5})^3 (\frac{P}{5})}{(\frac{3P}{5})^2}$

$= \frac{3P^2}{25}$

Answer: D

8 The following reaction is used industrially to produce a combustible gas from coal.

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$$

A mixture of powdered coal and steam at a pressure of 1 atm was allowed to reach equilibrium at a constant temperature of 500 K. At equilibrium, the total pressure had increased to 1.9 atm.

What is the numerical value of the equilibrium constant, K_p, at 500 K?

A 1.9 **B** 3.24

C 8.1 **D** 81

	$H_2O(g) + C(s)$	$\rightleftharpoons H_2(g)$	$+ CO(g)$
Initial/atm	1	0	0
Change/atm	−x	+x	+x
Eqm/atm	1−x	x	x

Total pressure = 1.9 = 1−x + x + x = 1 + x
x = 0.9
Partial pressure of H_2O = 0.1atm
Partial pressure of H_2 = Partial pressure of CO = 0.9atm
$K_p = (0.9)^2/0.1$ = 8.1 atm
Answer: C

9 A pure sample of $NH_3(g)$ is introduced into an evacuated vessel of constant volume. This vessel is maintained at constant temperature such that the equilibrium below is established.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

The value of the final pressure is then found to be 40 % greater than if only NH_3 were present. What is the mole fraction of H_2 in the reaction mixture?

A 0.14 **B** 0.29
C 0.43 **D** 0.72

	$2NH_3(g)$	$\rightleftharpoons$	$N_2(g)$	+	$3H_2(g)$
Initial pressure	x		0		0
Change	−2y		+y		+3y
Eqm pressure	x−2y		y		3y

Final pressure is found to be 40 % greater than if only NH_3 were present. Hence final pressure is 1.4x.

Final pressure = 1.4x = x−2y + y + 3y = x + 2y
y= 0.2x

Partial pressure of H_2 at eqm = 3(0.2x) = 0.6x
Mole fraction of H_2 = $\frac{0.6x}{1.4x}$ = 0.43
Answer: C

10 Given the following reaction:

A (g) + **B** (g $\rightleftharpoons$ 2**C** (g) + 2**D** (g) $K_p = 2.10 \times 10^2$ atm^2

An equimolar mixture of **A** and **B** is allowed to reach equilibrium at 700 K. Determine the total pressure at equilibrium if the partial pressure of **C** at equilibrium is found to be 2.00 atm.

A 1.28 atm **B** 4 atm
C 4.28 atm **D** 4.56 atm

	A (g) + **B** (g	$\rightleftharpoons$	2**C** (g)	+	2**D** (g)
Intial pressure/atm	x x				
Change	−1 −1		+2		+2
Eqm pressure/atm	x−1 x−1		2		2

$K_p = 2.10 \times 10^2 = \frac{(2^2)(2^2)}{(x-1)^2}$

$210 = \frac{16}{(x-1)^2}$

$\sqrt{210} = \frac{4}{(x-1)}$

$14.491\ (x-1) = 4$

$14.491x - 14.491 = 4$

$x = 1.276$

Total pressure = 2(1.276 −1) + 2 + 2
4.56 atm

Answer: D

11 Given that the K_p for the following equilibrium is 125 at 65°C,

X(s) + 3**Y**(g) ⇌ 3**Z**(g)

What is the mole ratio of **Y** : **Z** at equilibrium at 65°C?

A 1 : 1
B 1 : 5
C 25 : 1
D 125 : 1

$K_p = \frac{(P_Z)^3}{(P_Y)^3} = \frac{(n_Z)^3}{(n_Y)^3} = 125$

$\frac{n_Z}{n_Y} = 5$

$N_Z : n_Y = 1 : 5$

Answer: B

12 An equilibrium can be represented by the following equation:

P(aq) + **Q**(aq) ⇌ 2**R**(aq) + **S**(aq)

In a certain mixture, the equilibrium concentration of **Q** is 10 mol dm^{-3}.
What will be the new equilibrium concentration of **Q** if 5 mol of pure **Q** is dissolved in the mixture?

A 15 mol dm^{-3}
B between 10 mol dm^{-3} and 15 mol dm^{-3}
C 10 mol dm^{-3}
D between 5 mol dm^{-3} and 10 mol dm^{-3}

When 5 mol of **Q** is dissolved in the mixture, **[Q]** is increased. Hence position of equilibrium of $\mathbf{P}(aq) + \mathbf{Q}(aq) \rightleftharpoons 2\mathbf{R}(aq) + \mathbf{S}(aq)$ will shift right, to partially remove **Q**. Hence the new equilibrium concentration of Q will be between 10 and 15 mol dm^{-3}.

Answer: B

13 Ammonia is manufactured industrially by the Haber Process as shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

The operating conditions are: 400 to 450 °C; a pressure of 200 atm; an iron catalyst

Which of the following statement(s) is/are **true** about the Haber process for the manufacture of ammonia?

1 At higher temperatures, the production of ammonia becomes thermodynamically less feasible.
2 At higher pressures, the yield goes down but the rate of production of ammonia is faster.
3 The presence of a catalyst shifts the equilibrium position to the right and increases the yield.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

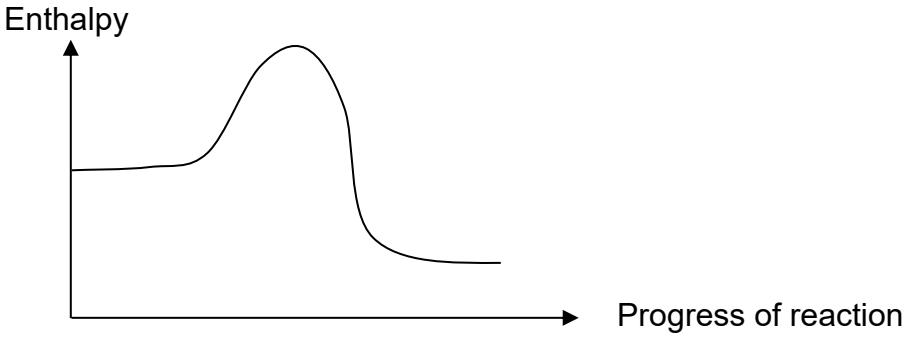
1✓ At higher temperature, the system will partially remove the heat by shifting position of equilibrium to the left.

2 × At higher pressure, the system will want to partially reduce the pressure by shifting to the side with less gas particles. Hence **position of equilibrium shift right**, **increasing the yield of ammonia**. Rate of production of ammonia increases with higher pressure.

3 × Catalyst does not cause equilibrium position to shift. It only increases the rate of forward and backward reaction.

Answer: D

14 The diagram below represents the reaction profile of the monomer-dimer system:



$$2NO_2\ (g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} N_2O_4\ (g)$$

brown colourless

Which statement about the equilibrium is correct?

A The equilibrium constant K_c will be larger at higher temperatures.

B k_f increases and k_b decreases when the equilibrium mixture is heated.

C Doubling the total pressure of the system reduces the percentage dissociation to half.

D At higher temperature, the colour intensity of the mixture increases.

A ✗ Reaction is exothermic as it involves the formation of dimer (ie. bonds formation). When temperature is increased, system will remove some heat by favouring endothermic reaction. Hence equilibrium position shifts left and K_c will be smaller.

B ✗ Both k_f and k_b increase when the equilibrium mixture is heated.

C ✗ When total pressure is doubled, equilibrium position shifts right to reduce the number of gas particles. However since equilibrium constant is the same, percentage dissociation is still the same

D ✓ At higher temperature, equilibrium position shifts right, producing more brown NO_2. Hence colour intensity of the mixture increases.

Answer: D

15 Ammonia is manufactured in the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92 \text{ kJ mol}^{-1}$$

Given that K_p for the above reaction is 3.375 at T K, which of the following statements involving the reaction is correct?

1 The partial pressure of H_2 (g) at equilibrium at T K can be expressed as $\frac{2}{3}\left(P_{NH_3}\right)^{2/3}\left(P_{N_2}\right)^{-1/3}$

2 When equilibrium is established, temperature, T K, is given by $T = \frac{\Delta H}{\Delta S}$

3 When pressure is increased, the yield of ammonia and the equilibrium constant increases

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

1 ✓ $K_p = \frac{P_{NH_3}{}^2}{(P_{N2})(P_{H2})^3} = 3.375$

$(P_{H2})^3 = \frac{P_{NH_3}{}^2}{(P_{N2})3.375}$

$P_{H2} = \frac{P_{NH_3}{}^{2/3}}{(P_{N2})^{\frac{1}{3}}(3.375)^{1/3}}$

$= \frac{2}{3}(P_{NH3})^{2/3}(P_{N2})^{1/3}$

2 ✓ At equilibrium $\Delta G = 0$

$\Delta H = T\Delta S$

Hence $T = \frac{\Delta H}{\Delta S}$

3 ✗ When pressure is increased, equilibrium position will shift right to reduce number of gas particles. Yield of ammonia will increase. Equilibrium constant remains the same as temperature remains.

Answer: B

16 The values of the equilibrium constant, K_p, for the reaction

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

are 0.313 kPa and 115 kPa at 25 °C and 727 °C respectively.
What deduction can be made from the information given above?

A The yield of CO_2 can be increased by adding some Ag_2CO_3 to a system already in equilibrium.
B The activation energy of the reverse reaction is higher than that of the forward reaction.
C Less CO_2 is formed at equilibrium if the reaction is allowed to take place in another container of a smaller volume.
D More CO_2 is formed at equilibrium if a suitable catalyst is used.

When temperature increases, K_p increases.
⇒ equilibrium position shifts right
⇒ System will remove some heat by favouring endothermic reaction
⇒ forward reaction is endothermic

A✗ Solid does not cause the equilibrium position to shift.
B✗ Cannot be deduced.
C✓ When volume decreases, pressure is increased. System will reduce the pressure partially by reducing number of gas particles. Equilibrium position shifts left and hence less CO_2 is formed.
D✗ Catalyst only speeds up rate of forward and backward reaction and does not affect yield of CO_2.
Answer: C

17 A system at equilibrium is subjected to the following changes separately:
(i) The pressure is reduced at constant temperature
(ii) The temperature is increased at constant pressure
For which equilibrium will both of these changes result in an increase in the proportion of products?

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = +53$ kJ mol^{-1}
B $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -950$ kJ mol^{-1}
C $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ mol^{-1}
D $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol^{-1}

When pressure is reduced, system will increase the pressure partially by increasing the number of gaseous particles.
Hence number of gaseous products > number of gaseous reactants
B or **D**

When temperature is increased, system will absorb some heat by favouring endothermic reaction.
Henceforward reaction should be endothermic.
Answer: D

18 When steam is passed over white hot coke, a mixture of combustible gases is obtained.

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g); \qquad \Delta H = +131 \text{ kJ mol}^{-1}$$

When equilibrium has been established, which of the following correctly describes what would happen if a proposed change is made to this system?

	proposed change	value of K_c	forward rate constant	backward rate constant
1	add catalyst	no change	increase	increase
2	add more C(s)	no change	increase	no change
3	increase temperature	increase	increase	decrease

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

1✓
2✗ Cu is reactant and not a catalyst. Hence the rate of reaction is not affected.
3✗ Increase in temperature will cause the system to absorb some heat favouring endothermic reaction. Hence equilibrium position will shift right. Kc will increase. An increase in temperature will cause both the forward and backward rate constant to increase (but to different extent).

Answer: D

19 Phosphorus pentachloride, PCl_5, is prepared from the chlorination of PCl_3 according to the equation below.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g); \qquad \Delta H = -124 \text{ kJ mol}^{-1}$$

At a constant temperature and a total initial pressure of 2.4 atm, a 1 : 2 mixture of PCl_3 and Cl_2 is allowed to reach equilibrium in a sealed vessel. The percentage yield is found to be 40%.

Which of the following are correct?

1 PCl_5 has a trigonal bipyramidal shape.
2 The equilibrium constant, K_p, is found to be 0.521 atm^{-1}.
3 When the total volume of the vessel is increased, the percentage yield decreases.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

1 ✓ 5bp 0lp around P ⇒ trigonal bipyramidal shape

2 ✓ Initial pressure of PCl_3 = 1/3 x 2.4 = 0.8 atm
Initial pressure of Cl_2 = 2/3 x 2.4 = 1.6 atm

	$PCl_3(g)$	+ $Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
Initial/atm	0.8	1.6		0
Change	$-(08)(\frac{40}{100})$ = −0.32	−0.32		+0.32
Eqm/atm	0.48	1.28		0.32

$$K_p = \frac{0.32}{0.481.28} = 0.521 \text{ atm}^{-1}$$

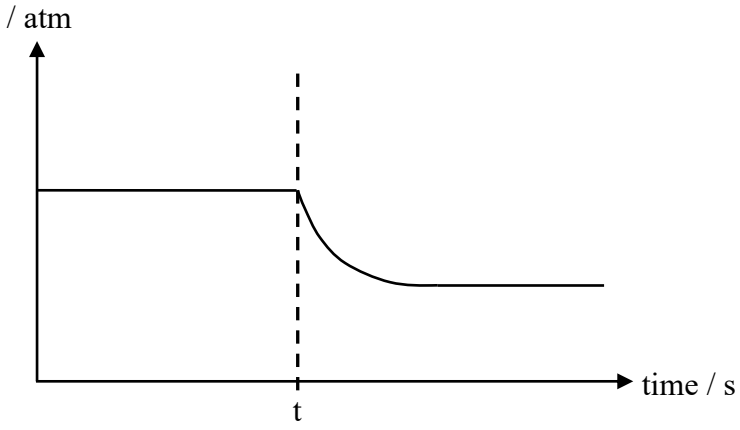
3 ✓ When total volume of vessel is increased, total pressure decreases.
System will partially reduce pressure by reducing number of gas particles.
Equilibrium position shifts to the left. Hence percentage yield decreases.

Answer: A

20 A sealed vessel of fixed volume contains a mixture of CO(g), H_2(g) and CH_3OH(l) at equilibrium.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) \qquad \Delta H < 0$$

At time t, the reaction mixture is subjected to a change. The graph below shows the partial pressure of CO against time.



Which changes, when carried out separately, could have given the graph above?

1 addition of H_2(g)
2 removal of some CH_3OH(l)
3 decrease in temperature

A 1, 2 and 3
B 1 and 2 only
C 1 and 3 only
D 3 only

K_c (and K_p) expression of heterogeneous equilibrium exclude the concentration (or partial pressure) of pure solids and pure liquids because they are constant at a given temperature. Hence, the removal of some liquid CH_3OH will not change its concentration and has no effect on the position of equilibrium. ⇒ Statement 2 is not correct

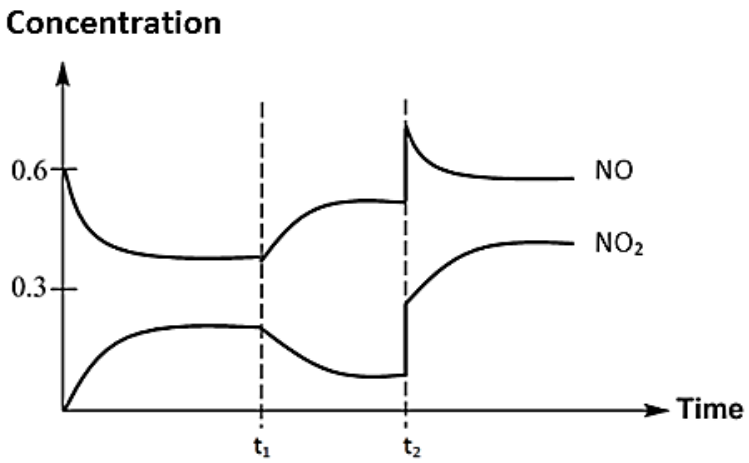
Addition of H_2(g) and a decrease in temperature will cause the position of equilibrium to shift to the right, lowering the partial pressure of CO(g).
⇒ Statements 1 and 3 are correct

Answer: C

21 At temperature T, 0.60 mol dm^{-3} of NO and 0.30 mol dm^{-3} of O_2 were introduced into a 2 dm^3 vessel and allowed to reach equilibrium.

$$2\ NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2\ (g) \qquad \Delta H < 0$$

The graph below shows the changes in the amounts of NO and NO_2 in the system with time. A change was made to the system at time $\mathbf{t_1}$ and $\mathbf{t_2}$.



What were the changes made at time $\mathbf{t_1}$ and $\mathbf{t_2}$?

	$\mathbf{t_1}$	$\mathbf{t_2}$
A	The temperature was increased	Volume of the system is increased
B	The temperature was decreased	More O_2 was added
C	An inert gas was added at constant volume	More NO_2 was added
D	The temperature was increased	Volume of the system is decreased

As the reaction is exothermic, an increased in the temperature at t_1 will favour the endothermic reaction to absorb some heat hence position of equilibrium shifts to the left.

At t_2, the pressure of the vessel is increased which shift the position of equilibrium to the right to reduce the number of gaseous molecules.

Answer: D

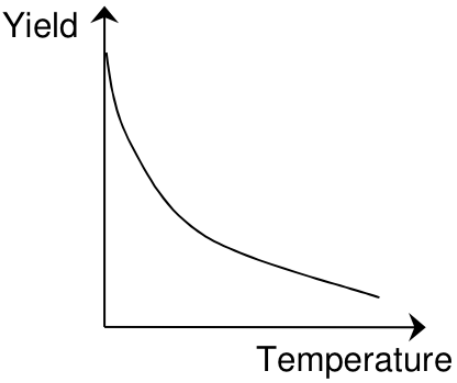
22 *Use of the Data Booklet is relevant to this question.*

Ammonia can be synthesised directly using a mixture of hydrogen gas and nitrogen gas in a reversible reaction as shown:

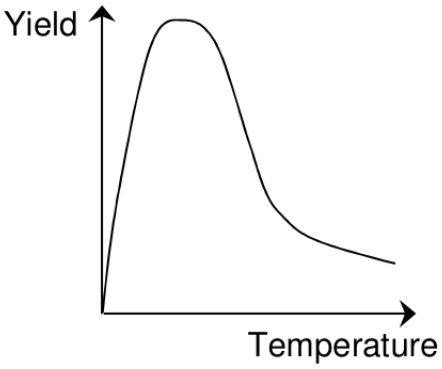
$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

Which one of the following describes the change in yield of ammonia at equilibrium as temperature increases?

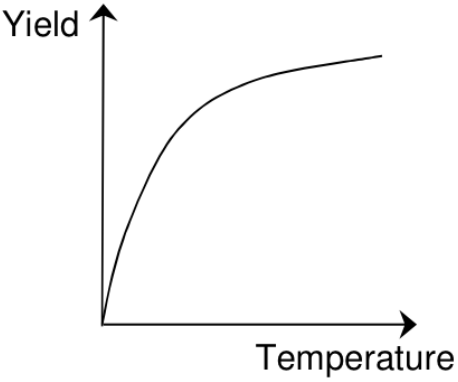
A



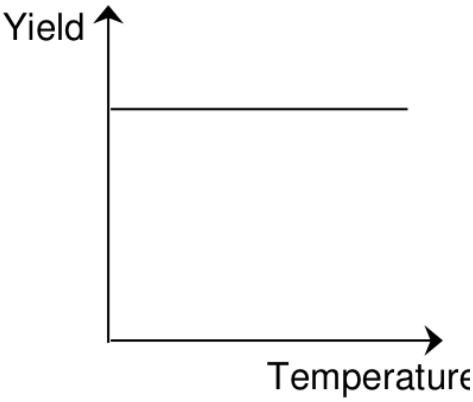
B



C



D



Using bond energies from Data Booklet

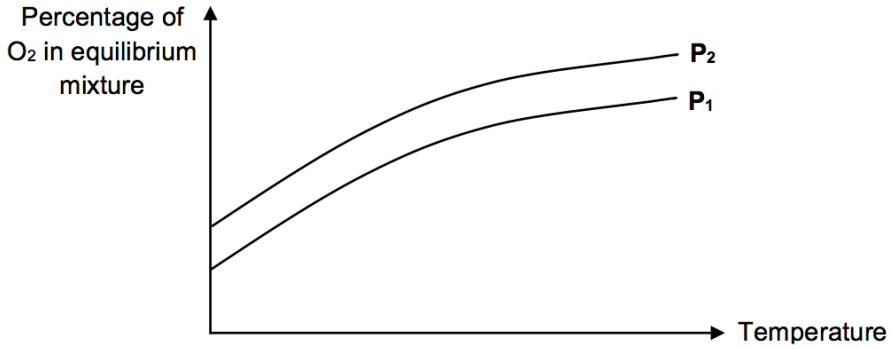
ΔH = 3(436) + 944 − 6(390) = −88 kJ mol^{-1}

When temperature increases, system will remove some heat by favouring endothermic reaction. Equilibrium position shifts left. Yield of ammonia decreases.

Answer: A

23 The graph below shows how the percentage of oxygen gas in the equilibrium mixture shown below varies with temperature at pressures $\mathbf{P_1}$ and $\mathbf{P_2}$.

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$



Which of the following statements about the reaction are correct?

1 The pressure $\mathbf{P_1}$ is larger than $\mathbf{P_2}$.
2 The forward reaction is exothermic.
3 Addition of an inert gas into the system will not cause the graph to shift.

A **1,2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

$\mathbf{P_1} \rightarrow \mathbf{P_2}$, % O_2 increases
⇒ Equilibrium position shift left
⇒ Gas particles in reactants > gas particles in products
⇒ There is a decrease in the total pressure, such that the system increases pressure partially by increasing number of gas particles.
⇒ Hence, $\mathbf{P_1} > \mathbf{P_2}$
1 ✓

When temperature increases, % O_2 in equilibrium mixture increases.
⇒ Equilibrium position shift left.
⇒ An increase in temperature will cause system to absorb some heat by favouring endothermic reaction.
⇒ Hence, backward reaction is endothermic (or) forward reaction is exothermic
2 ✓

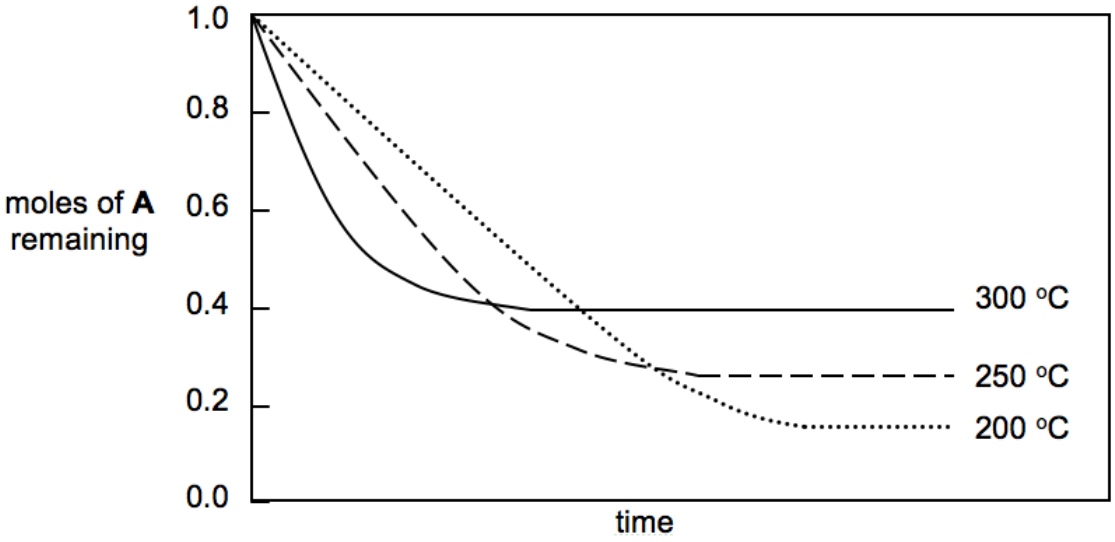
Addition of an inert gas into the system will not cause the graph to shift.
3 ✓

Answer: A

24 Gas **A** decomposes to two other gases, **B** and **C**, according to the following equation:

$$2\mathbf{A}(g) \rightleftharpoons 3\mathbf{B}(g) + \mathbf{C}(g)$$

The graph below shows the decomposition of 1.0 mol of pure gas **A** in the presence of a catalyst at various temperatures.



Which one of the following statements about the above system is **incorrect**?

A The decomposition of **A** is endothermic.
B The K_p of the system decreases with increasing temperature.
C The percentage decomposition of **A** is 60 % at 300 °C.
D The system becomes more disordered when it reaches equilibrium state.

When temperature decreases, less moles of A remains.
⇒ more A has undergone decomposition
⇒ equilibrium position shifts right
⇒ system will release some heat to favour exothermic reaction
⇒ forward reaction i.e. decomposition of **A** is exothermic
A ✗

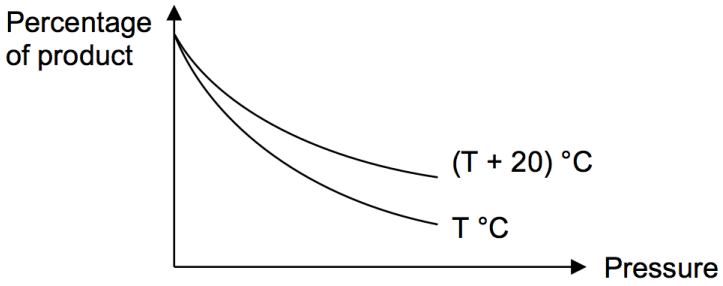
B ✓ K_p of the system increases with increasing temperature

C ✓ 0.4 mol of A is remaining ⇒ 0.6 mol of A has decomposed.
i.e. $\frac{0.6}{1.0} \times 100 = 60\%$

D ✓ The system becomes more disordered as there are more gas particles for products than reactants (4 mol vs 2 mol)

Answer: A

25 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



A $4Fe\,(s) + 3O_2\,(g) \rightleftharpoons 2Fe_2O_3\,(s)$ $\otimes H = -1644$ kJ mol^{-1}

B $2C\,(s) + O_2\,(g) \rightleftharpoons 2CO\,(g)$ $\otimes H = -222$ kJ mol^{-1}

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\otimes H = +57$ kJ mol^{-1}

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\otimes H = +86$ kJ mol^{-1}

When temperature increases, percentage of products increase.
⇒ When temperature increases, system will partially absorb some heat by favouring endothermic reaction. Since % of products increase, equilibrium position shifts right. Hence forward reaction is endothermic.
Either **C** or **D**.

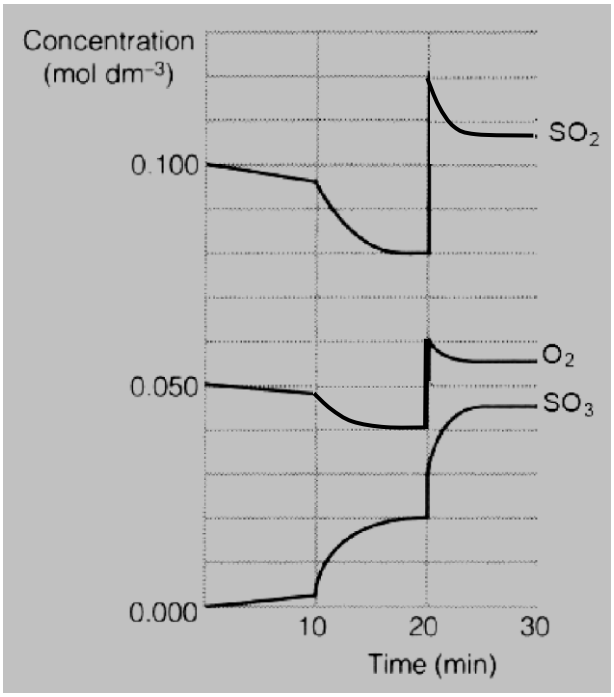
When pressure decreases, percentage of products increase.
⇒ When pressure decreases, system will partially increase pressure by increasing number of gas particles. Since % of products increase, equilibrium position shifts right. Hence, no. of gas particles for products > no. of gas particles of reactants.

Answer: C

26 During the Contact process, sulfur dioxide is converted to sulfur trioxide as shown by the equation below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ \Delta H = -197\ kJ\ mol^{-1}$$

The graph below shows how the concentration of the three gases changed when a series of changes was made.



Which conclusion can be drawn from this information?

A At 10 min, some sulfur dioxide gas was removed from the system.

B At 20 min, the numerical value of the equilibrium constant, K_c, was 1.56.

C At 20 min, the pressure of the system was decreased by increasing the volume.

D The temperature of the mixture at 30 min was higher than that at 20 min.

A ✗ There is no sharp decrease in concentration to represent the removal of SO_2.

B ✓ $K_c = \frac{0.02^2}{0.040.08^2} = 1.56$

C ✗ If pressure of the system is decreased, there should be a sharp decrease in all the concentration.

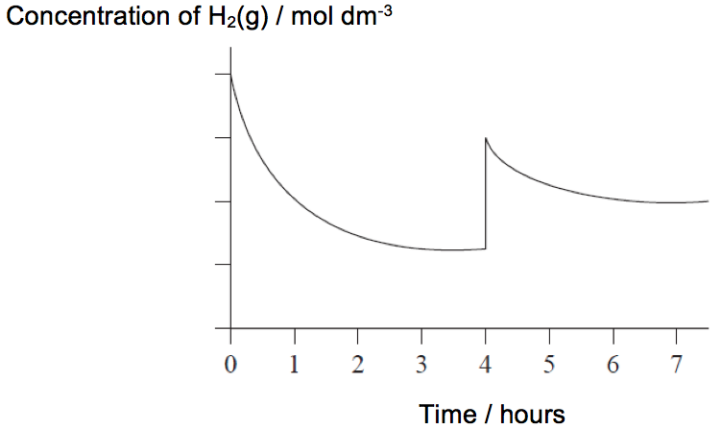
D ✗ If temperature of the mixture at 30 min was higher than that at 20min, system will partially absorb some heat to favour endothermic reaction. Equilibrium position will shift left. $[SO_2]$ and $[O_2]$ should increase, and $[SO_3]$ should decrease.

Answer: B

27 The reaction between phosphorus and hydrogen can result in the formation of phosphine as shown:

$$P_4(s) + 6H_2(g) \rightleftharpoons 4PH_3(g)$$

The graph shows the change in concentration of hydrogen for this reaction in which the system was disturbed after four hours.



Which of the following could explain the change in the hydrogen concentration at time, t = 4 hours?

A The volume of the reaction vessel was decreased.
B A catalyst was added.
C The pressure on the reaction mixture was decreased.
D More phosphorus was added.

A ✓ When volume of vessel was decreased, $[H_2]$ was increased. Equilibrium position shifted right to reduce $[H_2]$ partially.

B ✗ Adding a catalyst does not cause equilibrium position to shift.

C ✗ When the pressure of the reaction mixture was decreased, system will partially increase the pressure by shifting equilibrium position to the left. $[H_2]$ should increase.

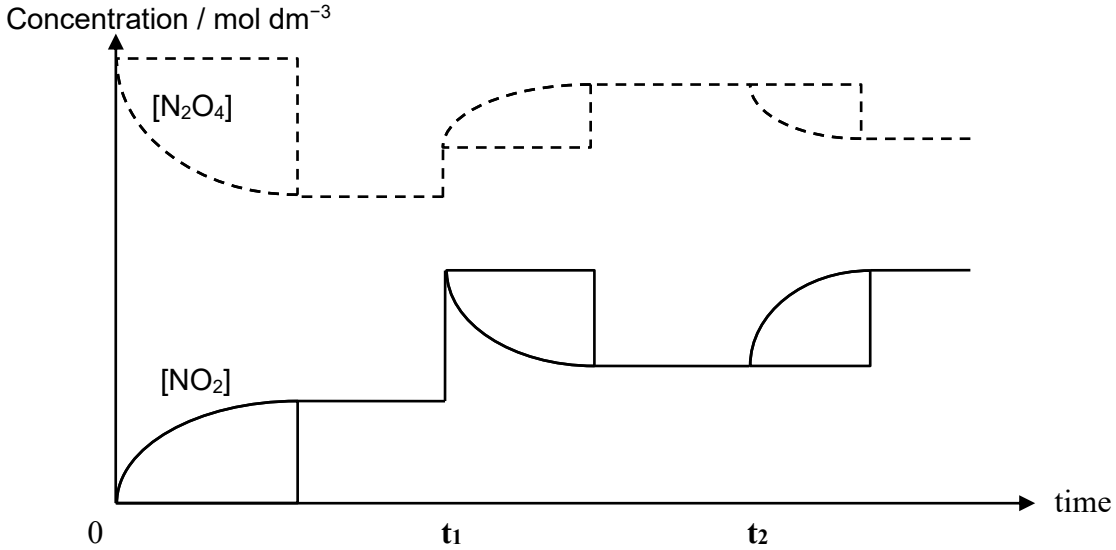
D ✗ Adding solid phosphorus does not cause equilibrium position to shift.

Answer: A

28 Consider the following equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

A certain amount of N_2O_4 was placed in a closed vessel and allowed to reach equilibrium.



Two changes were made to the equilibrium system at t_1 and t_2.

Using the graph above, what are the changes made at t_1 and t_2?

	t_1	t_2
A	[NO_2] increase	[N_2O_4] decrease
B	Pressure increase	[N_2O_4] decrease
C	Volume of vessel decrease	Temperature increase
D	Catalyst added	Temperature increase

At t_1, [NO_2] and [N_2O_4] increase sharply ⇒ volume of the vessel has been reduced.
At t_2, when temperature is increased, the system will absorb some heat. Equilibrium position will shift right to favour endothermic reaction. Hence, [NO_2] will increase and [N_2O_4] will decrease.

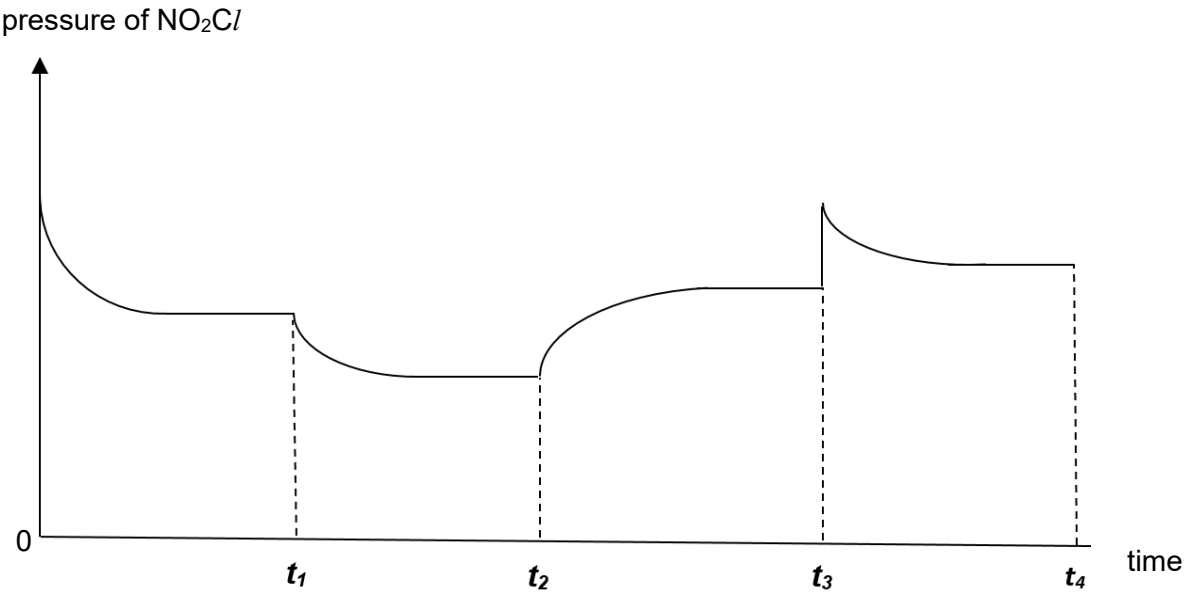
Answer: C

29 Nitrosyl chloride, NOC*l*, is a yellow gas that can be formed between nitryl chloride, NO_2Cl, and nitric oxide, NO, in the following reaction.

$$NO_2Cl(g) + NO(g) \rightleftharpoons NOCl(g) + NO_2(g) \qquad \Delta H < 0$$

NO_2Cl and NO were initially allowed to react in a closed vessel at 800 K and equilibrium was established.

The graph below shows how the pressure of NO_2Cl varied with time.



What could be the changes made to the system at t_1, t_2 and t_3?

	t_1	t_2	t_3
A	NO_2Cl was removed	temperature was increased	NO_2Cl was added
B	temperature was decreased	NO_2Cl was added	NO_2 was added
C	NO_2 was removed	temperature was increased	NO_2Cl was added
D	NO_2Cl was removed	NO_2Cl was added	temperature was decreased

At t_1: When NO_2 was removed, the position of equilibrium shifts right to produce more NO_2, causing the amount and hence pressure of NO_2Cl to decrease.

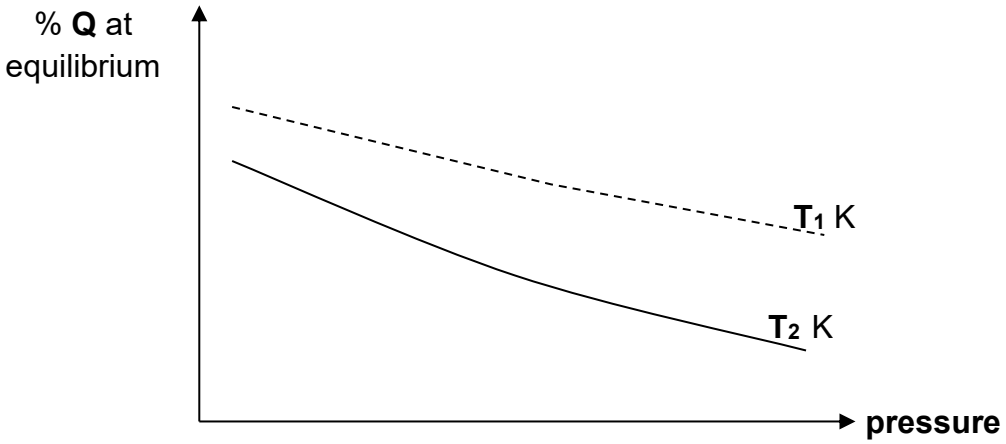
At t_2: when the temperature was increased, the position of equilibrium shifts left to favour the endothermic reaction by absorbing some heat. This causes the pressure of NO_2Cl to increase.

At t_3: when more NO_2Cl was added, it led to a sharp increase in pressure. The position of equilibrium then shifts right to counter act the change, leading to a decrease in the pressure of NO_2Cl.

Answer: C

30 The graph below shows the variation of the percentage of **Q** present at equilibrium, with temperature and pressure.

$$3O_2\,(g) + 4NH_3\,(g) \rightleftharpoons 2N_2\,(g) + 6H_2O\,(g) \qquad \Delta H = -1248\ kJ\ mol^{-1}$$



Which of the following systems could **Q** represent?

	Q	Temperature
A	O_2	$T_1 > T_2$
B	NH_3	$T_2 > T_1$
C	N_2	$T_1 > T_2$
D	H_2O	$T_2 > T_1$

$3O_2(g) + 4NH_3(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$ $\Delta H = -1248\ kJ\ mol^{-1}$
When pressure increases, equilibrium position shifts left to reduce the numbr of moles of gas to decrease pressure partially.
Therefore, Q represents products since the graphs show decreasing %Q when pressure increases.
Since forward reaction is exothermic, $T_2 > T_1$. By Le Chatelier's Principle, the equilibrium position shifts left towards the endothermic reaction to absorb some heat.
T_2 has lower %Q than T_1
Answer: D

31 The following process is used to convert methane to hydrogen.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H > 0$$

What will increase the yield of the reaction?

1 Increasing the temperature.

2 Increasing the total pressure by decreasing the total volume at constant temperature.

3 Removing CO and H_2 gas as they are formed but keeping the total volume of the mixture the same.

A 1 **B** 1 and 3 **C** 2 and 3 **D** 3

Option 1 ✓: Increasing the temperature causes equilibrium position to shift to the right as the forward endothermic reaction removes some of the added heat.

Option 2 ✗: Increase in total pressure will cause equilibrium position to shift left to remove the added pressure as the backward reaction results in a decrease in number of gaseous particles.

Option 3 ✓: Removing CO and H_2 causes equilibrium position to shift right to partially increase the concentration of CO and H_2 or decreases the total pressure of the system, thus P.O.E. shifts right.

Answer: B

Answers: Chemical Equilibrium Structured Questions

1(a) $pV = nRT = (m/M)RT$
$(101 \times 10^3)(10 \times 10^{-3}) = (m / 20)(8.31)(150 + 273)$
$m = 5.75$ g

(b) Let the initial amt of N_2H_4 be a.

(i)

	$N_2H_4(g)$	$\rightleftharpoons$	$N_2(g)$	+	$2H_2(g)$
initial amt / mol	a		0		0
eqm amt / mol	$a(1-\alpha)$		$a\,\alpha$		$2a\,\alpha$

Total amt of gases present at eqm
$= a(1-\alpha) + a\alpha + 2a\,\alpha = a(1+2\,\alpha)$ mol

$$\text{average } M_r = \frac{1-\alpha}{1+2\alpha} M_r(N_2H_4) + \frac{\alpha}{1+2\alpha} M_r(N_2) + \frac{2\alpha}{1+2\alpha} M_r(H_2)$$

$$20 = \frac{1-\alpha}{1+2\alpha}(32.0) + \frac{\alpha}{1+2\alpha}(28.0) + \frac{2\alpha}{1+2\alpha}(2.0)$$

$\alpha = 0.30$

(ii)
$$p_{N_2H_4} = \chi_{N_2H_4} p_T = \frac{1-\alpha}{(1+2\alpha)} p_T = \frac{1-0.3}{(1+0.6)}(1) = 0.4375\,\text{atm}$$ = 0.438 atm

$$p_{N_2} = \chi_{N_2} p_T = \frac{\alpha}{(1+2\alpha)} p_T = \frac{0.3}{(1+0.6)}(1) = 0.1875\,\text{atm}$$ = 0.188 atm

$$p_{H_2} = \chi_{H_2} p_T = \frac{2\alpha}{(1+2\alpha)} p_T = \frac{2(0.3)}{(1+0.6)}(1) = 0.375\,\text{atm}$$

$$K_P = \frac{p_{N_2} p^2_{H_2}}{p_{N_2H_4}} = \frac{(0.1875)(0.375)^2}{0.4375} = 6.03 \times 10^{-2}\ \text{atm}^2$$

(iii) α will decrease.

2 (i)
$$K_p = \frac{p_{CO} p_{H_2}}{p_{H_2O}}$$ Units: atm

(ii)
$$K_p = \frac{p_{CO} p_{H_2}}{p_{H_2O}} = \frac{6.14^2}{2.67}$$ =14.1 atm

(iii) When temperature is increased from 25 °C to 800 °C, K_p increases, which means the product-reactant ratio increases. Temperature increase also favours the endothermic reaction and shifts the equilibrium position to the right hence producing more CO and H_2.

3(i)
$$K_p = \frac{[I_3^-]}{[I_2][I^-]}$$ Units: $mol^{-1}dm^3$

(ii)

	I_2	+ I^-	⇌	I_3^-
Initial /mol	**0.080**	**0.058**		**0**
Change /mol	**−0.0375**	**−0.0375**		**+0.0375**
Eqm /mol	**0.0425**	**0.0205**		**0.0375**

$K_c = \frac{(\frac{0.0375}{0.5})}{(\frac{0.0425}{0.5})(\frac{0.0205}{0.5})}$ = 21.52 $mol^{-1}dm^3$

4 (i)

	$ClNO_2$(g) +	NO(g) ⇌	NO_2(g) +	ClNO(g)
Initial/ atm	1.5	1.5	0	0
Change/ atm	−0.93	−0.93	+0.93	+0.93
Eqm/ atm	0.57	0.57	0.93	0.93

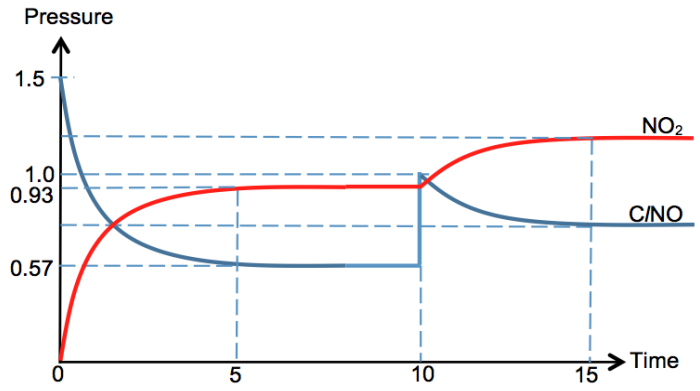
$$K_p = \frac{P(NO_{2)}P(ClNO)}{P(ClNO_2)P(NO)}$$

$$K_p = \frac{(0.93)^2}{(0.57)^2}$$

K_p = 2.67 (no units)

(ii) By LCP, the position of the equilibrium will shift forward to consume some of the extra C*l*NO$_2$ in the reaction to partially decrease its partial pressure.

(iii)



5
(a)(i) $K_p = \dfrac{(p_{O_2})^3}{(p_{O_3})^2}$

(ii) At r.t.p, atmospheric pressure = 101325 Pa
By Dalton's law of partial pressure,
Partial pressure of O_2 = (0.21 × 101325) Pa = 21 278 Pa ≈ 21300 Pa

(iii) $P_{O3} = 1.551 \times 10^{-8}$

(b) The K_p for the equilibrium reaction increases drastically when the temperature is increased from 298 K to 2000 K.
Exhaust gas from cars contains NO gas because of the reaction between atmospheric nitrogen and oxygen in the hot internal combustion car engine.
Exhaust gas will contain a high proportion of NO gas as forward reaction is favoured due to an endothermic enthalpy change.

6

	PC*l*$_3$(g) + C*l*$_2$(g) ⇌ PC*l*$_5$(g)		
initial partial pressure / atm	1.9	1.9	0
Δ in partial pressure / atm	– 1.68	– 1.68	+ 1.68
eq^m partial pressure / atm	0.220	0.220	1.68

(ii) % conversion of PC*l*$_3$ = 1.68 / 1.9 x 100% = **88.4%**

$$K_p = \frac{P_{PCl_5}}{(PCl_3)(P_{Cl_2})} = \frac{1.68}{0.22^2} = 34.7 \text{ atm}^{-1}$$

When the temperature is increased, the system will try to **absorb the heat** by Le Chatelier's Principle and hence, favouring an endothermic reaction. The position of equilibrium shifts to the left and therefore, the yield of PC*l*$_5$ will **decrease**.

2. ACID–BASE EQUILIBRIUM

Section A: Multiple Choice Question

1 The following reaction takes place using liquid ammonia as a solvent.

$$NaNH_2 + NH_4Cl \rightarrow NaCl + 2NH_3$$

Which statement best explains why this reaction should be classified as a *Bronsted–Lowry* acid–base reaction?

A NH_3 is basic.

B $NaCl$ is neutral.

C NH_4Cl is a salt.

D NH_2^- is a proton acceptor.

2 Which correctly lists 0.10 mol dm^{-3} solutions of HCl, KCl, NH_4Cl, KOH and KCN in order of increasing pH?

A HCl, KCl, KCN, NH_4Cl, KOH

B HCl, NH_4Cl, KCl, KCN, KOH

C HCl, KCl, NH_4Cl, KCN, KOH

D KCl, KCN, KOH, HCl, NH_4Cl

3 Which statement is an **incorrect** description of a buffer solution?

A It must contain an equal amount of a weak acid and its conjugate base

B It may contain an amino acid.

C It resists pH change on slight dilution.

D It cannot resist pH change when large amount of acid is added.

4 The pH of an aqueous solution mixture containing equal amounts of ammonia and ammonium chloride is 9.26.

Which would happen when 2.0 cm^3 of 0.10 mol dm^{-3} nitric acid is added to the mixture?

A The pH of the resulting solution increases.

B The number of moles of NH_4^+ ions in the resulting solution increases.

C The number of moles of NH_3 molecules in the resulting solution remains unchanged.

D The molar ratio of NH_4^+ ions to NH_3 molecules in the resulting solution decreases.

5 Which of the following increase with decreasing temperature for the dissociation of water?

Temperature/ °C	K_w/ mol^2 dm^{-6}
50	5.5 x 10^{-14}
25	1.0 x 10^{-14}

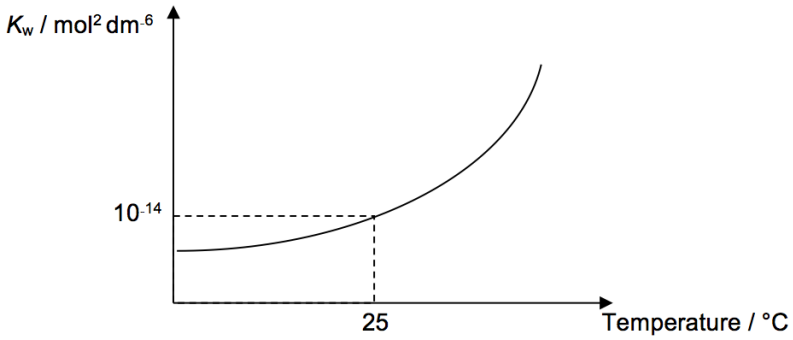
1 pK_b **2** pH **3** pK_w

A 3 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3 only

6 Water dissociates as shown:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, varies with temperature as shown in the graph below.



Assuming that [H_2O] = 55.6 mol dm^{-3}, which statements about the above equilibrium system are correct?

1 The pH of water decreases as temperature increases.
2 The concentrations of H^+ and OH^- are equal at all temperatures.
3 At 25 °C, K_a is numerically larger than K_w.

A 1 and 3 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3 only

7 Dimethyl sulfoxide, DMSO, is an organic solvent which can dissolve polar and non–polar compounds. Ethanoic acid ionises in DMSO in the following manner:

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$

The pK_a of ethanoic acid in DMSO is 12.6.

What is the concentration of H^+ ions at equilibrium if 1.0×10^{-2} mol of ethanoic acid was dissolved in 500 cm^3 of DMSO?

A 5.0×10^{-8} mol dm^{-3}

B 7.1×10^{-8} mol dm^{-3}

C 2.5×10^{-15} mol dm^{-3}

D 5.0×10^{-15} mol dm^{-3}

8 What is the K_a of ethanoic acid at 25 °C given that the pH of a 1.3×10^{-4} mol dm^{-3} solution of ethanoic acid was found to be 4.40?

A 3.33×10^{-4}

B 1.22×10^{-5}

C 1.76×10^{-5}

D 9.33×10^{-6}

9 25 % of ethanoic acid in a solution was converted to ethanoate ions by reaction with sodium hydroxide solution at 25 °C.

What is the K_a of ethanoic acid at 25 °C given that the pH of the solution was found to be 4.28?

A 1.57×10^{-4}

B 1.31×10^{-5}

C 1.75×10^{-5}

D 5.24×10^{-5}

10 The pH range and colour changes for two acid–base indicators are given below.

Indicator	pH range
X	violet 3.0 – 5.0 red
Y	yellow 5.6 – 7.6 blue

A solution in which X is red and Y is yellow is

A 0.1 mol dm^{-3} HCl

B 0.1 mol dm^{-3} CH_3COOH ($K_a = 1.8 \times 10^{-5}$ mol dm^{-3})

C 0.1 mol dm^{-3} HX($K_a = 2.5 \times 10^{-10}$ mol dm^{-3})

D 0.1 mol dm^{-3} NH_3 ($K_b = 1.8 \times 10^{-5}$ mol dm^{-3})

11 Which combination of solutions would give a buffer solution?

1 10 cm^3 of 0.1 mol dm^{-3} CH_3CO_2H and 10 cm^3 of 0.1 mol dm^{-3} CH_3CO_2Na

2 10 cm^3 of 0.1 mol dm^{-3} HC*l* and 20 cm^3 of 0.1 mol dm^{-3} CH_3CO_2Na

3 20 cm^3 of 0.1 mol dm^{-3} HC*l* and 10 cm^3 of 0.1 mol dm^{-3} $Mg(CH_3CO_2^-)_2$

A 1 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3 only

12 Which combinations of substances would give a buffer solution?

1 15.0 cm^3 of 0.05 mol dm^{-3} HNO_3 and 25.0 cm^3 of 0.1 mol dm^{-3} CH_3NH_2

2 20.0 cm^3 of 0.2 mol dm^{-3} CH_3COOH and 10.0 cm^3 of 0.5 mol dm^{-3} NaOH

3 25.0 cm^3 of 0.1 mol dm^{-3} HC*l* and 50.0 cm^3 of 0.05 mol dm^{-3} NH_3

A 1, 2 and 3 only
B 1 and 2 only
C 1 only
D 2 only

13 What is the pH of an aqueous solution containing 0.1 mol dm^{-3} sodium benzoate and 0.01 mol dm^{-3} benzoic acid? [K_a(benzoic acid) = 6 x 10^{-5} mol dm^{-3}]

A 3.22 **B** 4.22 **C** 4.78 **D** 5.22

14 What is the pH of a solution containing 100 cm^3 of 0.440 mol dm^{-3} ammonia and 100 cm^3 of 0.240 mol dm^{-3} of hydrochloric acid? [pK_b (ammonia) = 4.80 at 25 °C]

A 4.72 **B** 4.88 **C** 9.12 **D** 9.28

15 Methylamine, CH_3NH_2, is a weak base. When 40 cm^3 of 0.10 mol dm^{-3} HC*l* is added to 20 cm^3 of 0.30 mol dm^{-3} CH_3NH_2, the pH of the resulting solution obtained is 10.5.
Given K_w = 1.00 × 10^{-14} mol^2 dm^{-6}, what is the pK_b of methylamine, CH_3NH_2?

A 3.20 **B** 3.50 **C** 5.20 **D** 10.5

16 Human plasma is buffered mainly by dissolved CO_2 which has reacted to form carbonic acid.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Usually the pH of human plasma is 7.4. The acid dissociation constant, K_a, of carbonic acid is 7.90×10^{-7} mol dm^{-3}.

Which statement is **incorrect**?

A This buffer system can be prepared by mixing suitable amounts of sodium hydrogencarbonate and hydrochloric acid.

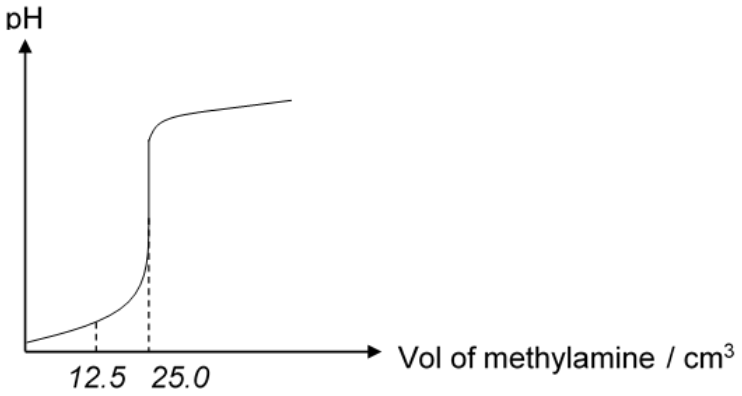
B The ratio of $[HCO_3^-]$ to $[H_2CO_3]$ in human plasma is 20 : 1.

C Its pH value remains constant when diluted with water.

D It has a pH value equal to the pK_a value of carbonic acid.

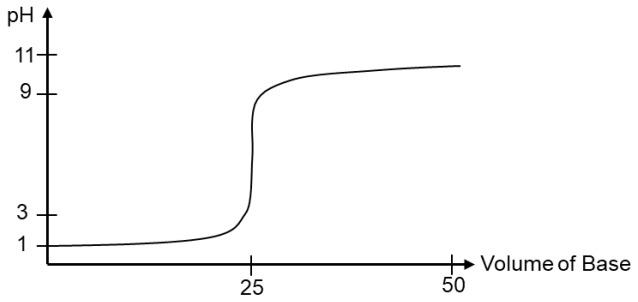
17 The graph below shows the pH changes when 25.0 cm^3 of 0.100 mol dm^{-3} aqueous HC*l* was titrated against 0.100 mol dm^{-3} methylamine.

What is the pH of the solution when 12.5 cm^3 of methylamine was added?
[K_b of methylamine = 4.37×10^{-4} mol dm^{-3}.]



A 1.48 **B** 2.90 **C** 3.36 **D** 10.6

18 The graph shows the change in pH when an aqueous base is gradually added to 25 cm^3 of an acid.



Which pair of solutions will give these results?

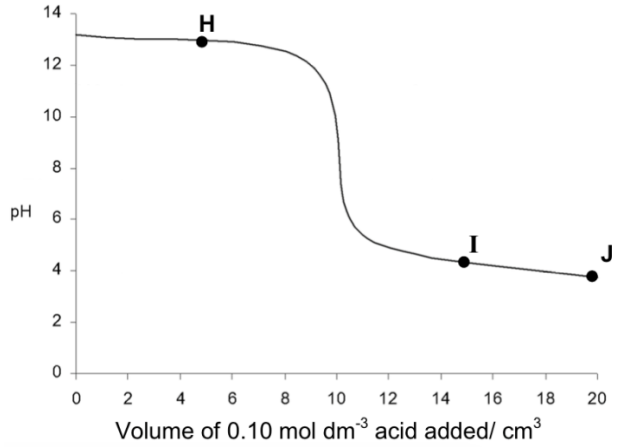
A 0.10 mol dm^{-3} HC*l* and 0.05 mol dm^{-3} NH_3

B 0.10 mol dm^{-3} HC*l* and 0.10 mol dm^{-3} NaOH

C 0.05 mol dm^{-3} H_2SO_4 and 0.10 mol dm^{-3} NH_3

D 0.10 mol dm^{-3} CH_3COOH and 0.10 mol dm^{-3} NaOH

19 The graph shows the change in pH when 0.10 mol dm^{-3} acid is gradually added to 10 cm^3 of 0.1 mol dm^{-3} sodium hydroxide.

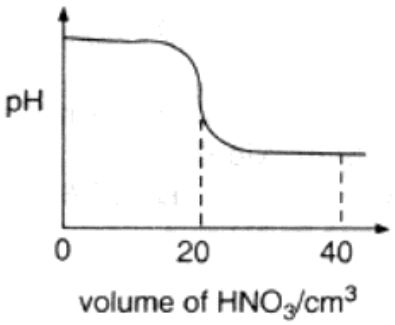


Which correctly identifies the acid used and the point on the curve at which maximum buffer capacity occurs?

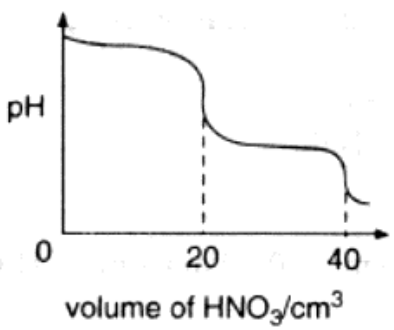
	Acid used	Maximum buffer capacity
A	HCN	**I**
B	H_2SO_4	**H**
C	HF	**J**
D	$(COOH)_2$	**I**

20 Which graph correctly represents the variation of pH against the volume of nitric acid added when 20.0 cm^3 of a 0.2 mol dm^{-3} sodium carbonate solution is titrated against 0.2 mol dm^{-3} nitric acid using phenolphthalein and methyl orange indicators?

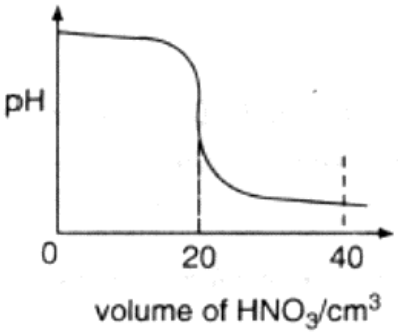
A



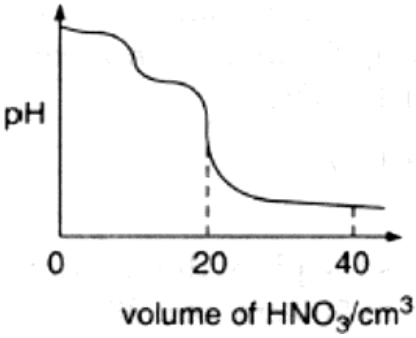
B



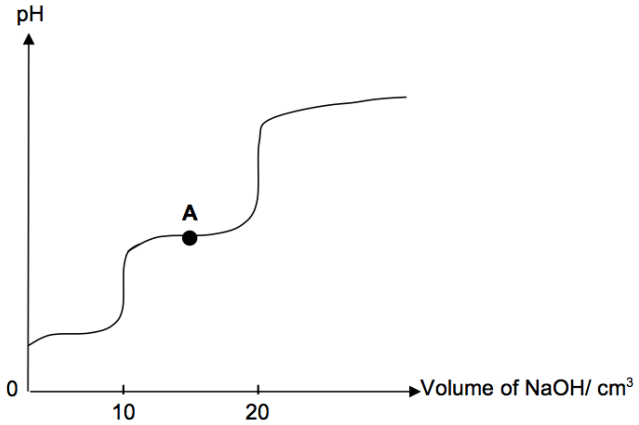
C



D



21 The titration curve below shows the reaction between a solution of 0.10 mol dm^{-3} weak acid, $H_2C_2O_4$, and 0.20 mol dm^{-3} aqueous sodium hydroxide.



Which statement is correct?

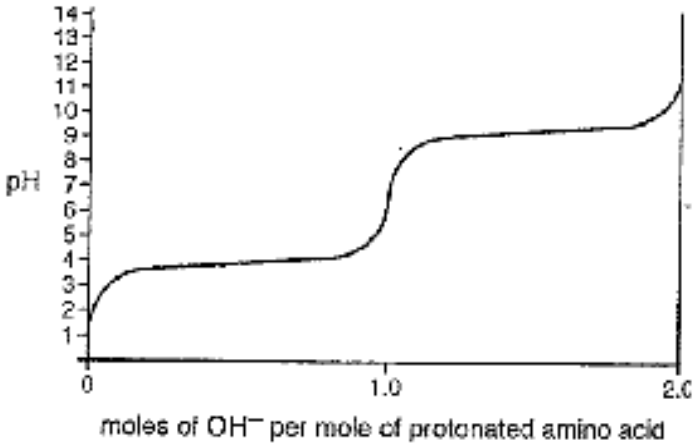
A Methyl orange cannot be used as an indicator in a titration to verify the concentration of $H_2C_2O_4$.

B The volume of $H_2C_2O_4$ used in this titration is 40 cm^3.

C There are equal amounts of $HC_2O_4^-$ and $C_2O_4^{2-}$ present at point **A**.

D The resultant solution formed has more H^+ than OH^- when 20 cm^3 of NaOH has been added.

22 The titration curve of NaOH with alanine, $H_2NCH(CH_3)COOH$, is as shown.



The two stages of titration are associated with two different dissociation constants, K_1 and K_2.
Which statements are always correct for alanine?

1 The form $H_2NCH(CH_3)CO_2^-$ is the most common species present at pH 7.

2 Equal concentrations of $H_3N^+CHRCO_2H$ and $H_3N^+CHRCO_2^-$ are present at pH = pK_1.

3 There is no net charge on the amino acid at the point when the slope of the curve is at a maximum at its centre.

A 1 and 2 only

B 1 and 3 only

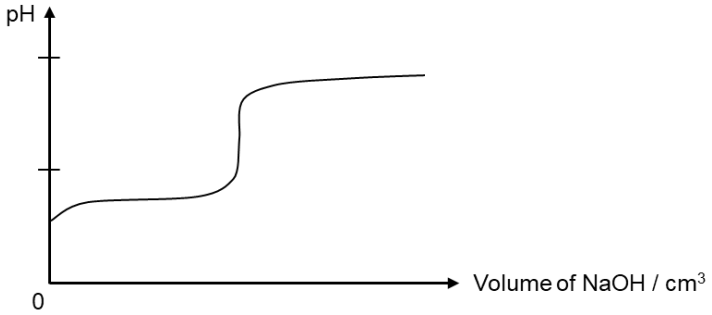
C 2 and 3 only

D 1, 2 and 3 only

B: Structured Question

1 Lactic acid, $CH_3CH(OH)CO_2H$ is an α–hydroxy acid (AHA) used as an important flavouring component of many foods such as cheese, yoghurt and pickled cabbage.

0.200 g of lactic acid (M_r = 90.0) was dissolved in 20.0 cm^3 water, and the solution was titrated with 0.100 mol dm^{-3} aqueous NaOH. The following titration curve was obtained. (K_a of lactic acid = 1.38 x 10 $^{-4}$ mol dm^{-3})



(i) Explain the term acid dissociation constant, K_a as applied to lactic acid.

(ii) Calculate the volume of NaOH required to reach the equivalence point in the titration.

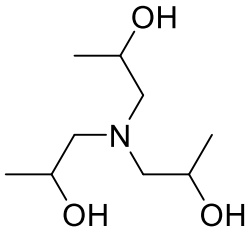
(iii) Calculate the pH of the solution at the equivalence point.

(iv) The table below lists the working ranges of some acid–base indicators.

Indicator	Working range	Low pH color	High pH color
Tetrabromophenol blue	3.0 – 4.6	yellow	blue
Methyl red	4.4 – 6.2	red	yellow
Bromothymol blue	6.0 – 7.2	yellow	blue
Cresol red	7.2 – 8.8	yellow	red
Thymolphthalein	9.3–10.5	colorless	blue

Suggest the best indicator that can be used for this titration and give a reason for your choice.

2 Triisopropanolamine (**TIPA**), $N(C_3H_6OH)_3$, is a monoprotic weak base which is used as a neutralising agent in agricultural products. The structure is shown below.



(a) **TIPA** is a *weak Bronsted base*. What do you understand by the terms in italics? [1]

(b) 20.0 cm^3 of a solution of **TIPA** was exactly neutralised by 25.00 cm^3 of 0.050 mol dm^{-3} hydrochloric acid.

(i) Suggest, with a reason, a suitable indicator for this titration.

(ii) Calculate the molar concentration of the solution of **TIPA**.

(iii) When 12.50 cm^3 of hydrochloric acid was added to the solution of **TIPA**, the pH of the resulting solution was 9.6. Calculate a value for the base dissociation constant, K_b, of **TIPA**.

(iv) Determine the initial pH of the solution of **TIPA**.

[6]

(c) **(i)** **TIPA** behaves similarly like NH_3. Write a chemical equation to show how **TIPA** can help in neutralising nitric acid in soil.

(ii) In terms of structure and bonding, explain why the product in **(c)(i)** has a higher melting point than that of **TIPA**.

[3]

(d) It was found that, besides the pH condition of soil, magnesium ion deficiency in the soil decreases the grain quality and protein content of the rice crop cultivated. Two soil samples with different amounts of magnesium hydroxide were then analysed for their suitability in rice crop cultivation.

(i) In the first sample, the pH of the soil is 8.7 and the concentration of $Mg^{2+}(aq)$ in the soil is found to be 0.0717 mol dm^{-3}.
Write an expression for the solubility product, K_{sp}, of magnesium hydroxide and calculate its value, including its units.

(ii) Hence, calculate the concentration of Mg^{2+} ions in the second sample of soil with pH 12.

(iii) Deduce whether the first or second soil sample would favour a good cultivation of rice crop.

(iv) Suggest how the product in **(c)(i)** helps in the uptake of Mg^{2+} by the rice crop.

[5]

3 Liquid hydrazine, N_2H_4, has alkaline properties comparable to those of ammonia but ammonia is fifteen times stronger.

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

(i) What feature of the hydrazine molecule enables it to act as a base?

(ii) Write an expression for the base dissociation constant, K_b of N_2H_4.

(iii) Given that the K_a value of $N_2H_5^+$ is 3.33 x 10^{-9} mol dm^{-3}, calculate the pH of 0.20 mol dm^{-3} of N_2H_4 at 25°C.

4 Mixtures of citric acid, $C_5H_7O_4CO_2H$ (K_a = 7.40 x 10^{-4} mol dm^{-3}), and its sodium salt are often used as acidity regulators for food. The mixture regulates the pH of food by acting as a buffer.

(a) Prove that the pH of a mixture formed from 25.0 cm^3 of 0.200 mol dm^{-3} citric acid and 2.48 g of sodium citrate (M_r = 198) is 3.53.

(b) When 0.059 g of an unknown solid was added to the mixture prepared in **(a)**, the pH of the resultant solution is 3.73. Determine the molar mass of the solid and hence suggest its identity.

(c) Determine the volume of 0.100 mol dm^{-3} of HC*l*(aq) that needs to be added to the solution in **(a)** to obtain a buffer at its maximum buffering capacity.

5 Many of the chemical reactions that occur in living systems are extremely sensitive to pH. As a result, the human body maintains a remarkably intricate system of buffers, both within tissue cells and in the fluids that transport blood cells. Blood is one of the most prominent examples of a buffer in the human body.

The major buffer system that is used to control the pH of blood is the carbonic acid hydrogen carbonate buffer system.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

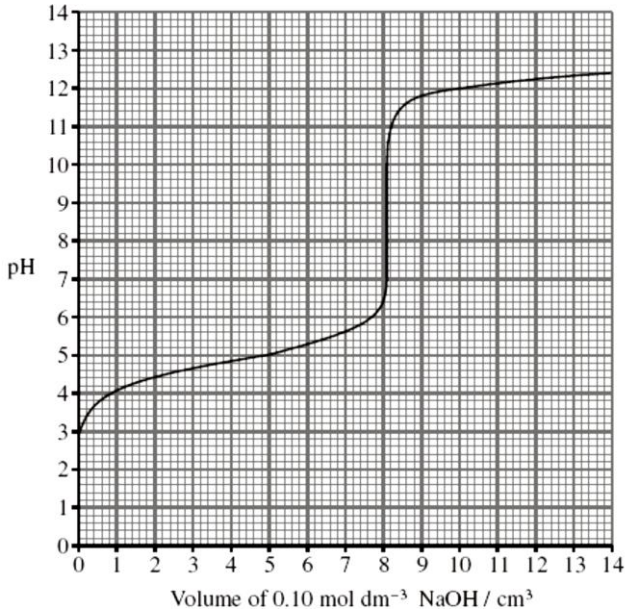
(i) Explain, with the aid of equations, how the buffer system in blood helps to control pH.

(ii) The pH of human plasma is usually maintained at about 7.4. Calculate the ratio of the concentrations of hydrogen carbonate ion and carbonic acid in plasma, given the pK_a of carbonic acid is 6.10.

(iii) Using your answer in **(ii)**, calculate the new pH of a 2.0 dm^3 of the human plasma, which is 0.05 mol dm^{-3} with respect to carbonic acid, when 0.03 mol of H^+ is added.

[6]

6 The following graph shows how the pH changes during the titration of 10 cm^3 of a solution of a weak acid(HA) with 0.10 mol dm^{-3} NaOH.



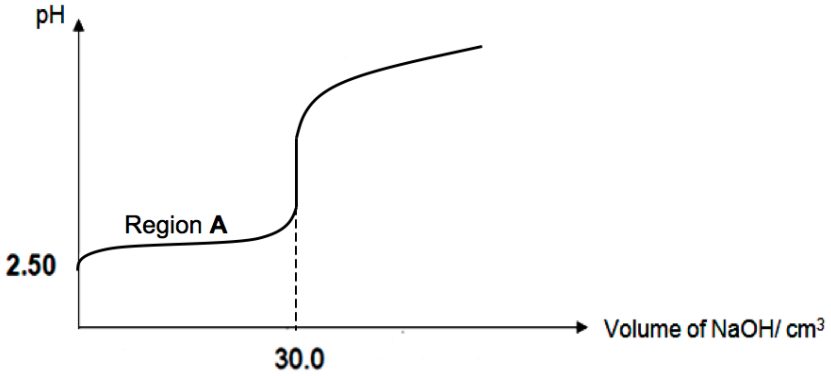
(a) State the pH at the equivalence point and explain why the pH changes rapidly in this region. [2]

(b) Calculate the initial concentration of the acid (HA). [1]

(c) Calculate the $[H^+]$ of the acid before any sodium hydroxide is added. Use this value to determine the K_a value and the pK_a value of the acid. [2]

7 Ethanoic acid, CH_3CO_2H, also commonly known as acetic acid, is an important chemical due to its varied uses in the industry.

The graph below shows the changes in pH when a 25.0 cm^3 sample of vinegar, with ethanoic acid as its main component, is titrated against 0.45 mol dm^{-3} aqueous sodium hydroxide.



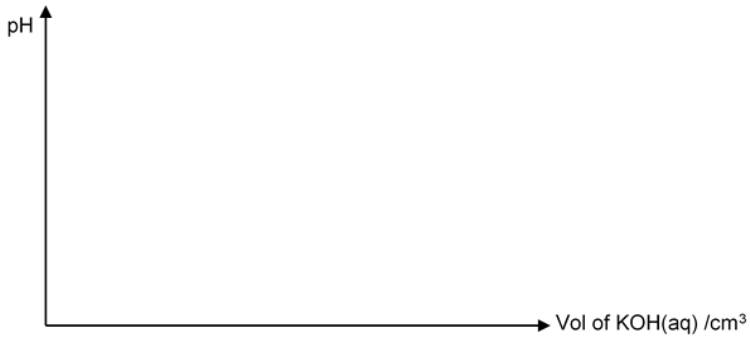
(i) Using the information provided, show by calculations that the acid dissociation constant, K_a of ethanoic acid has an approximate numerical value of 1.86×10^{-5}.

(ii) State a suitable indicator for this titration. Explain your choice.

8 The pK_b of cocaine is 5.59 at 25 °C. A 25.0 cm^3 sample of 0.500 mol dm^{-3} cocaine hydrochloride was titrated with aqueous KOH of the same concentration.

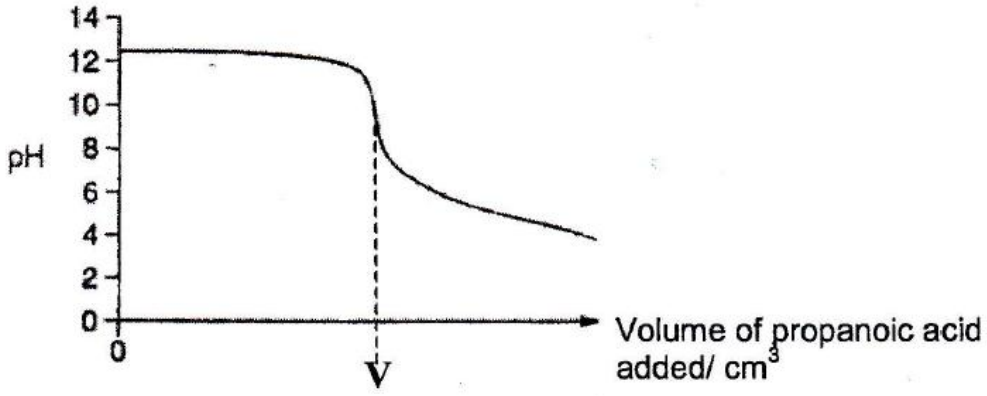
(i) Calculate the pH of the solution at the equivalence point.

(ii) Sketch a graph to show how the pH changes during this titration. Mark clearly on your sketch the pH values at maximum buffering capacity and at the equivalence point.



(iii) Explain why methyl orange cannot be used as an indicator in this titration. [5]

9 **(a)** A 0.031 mol dm^{-3} solution of a base, MOH, has a pH of 12.5. (**M** is a metal.)
25 cm^3 of the solution of MOH was titrated with 0.025 mol dm^{-3} propanoic acid, CH_3CH_2COOH, at 25 °C. The pH of the solution was followed using a pH meter and the following titration curve was obtained.
K_a of propanoic acid = 1.29 x 10^{-5} mol dm^{-3}



(i) Calculate the concentration of hydroxide ions present in the sample of MOH and use it to explain whether it is a strong or weak base. [1]

(ii) Calculate the value of **V**. [1]

(iii) Explain, with the aid of an equation, why the pH when **V** cm^3 of propanoic acid was added, is greater than 7. [2]

(b) The colour of blackberries is due to a compound known as cyanidin. Cyanidin is a weak organic acid which may be represented by CyH. In aqueous solution, CyH dissociates slightly:

$$\underset{\text{red}}{CyH\,(aq)} \rightleftharpoons \underset{\text{purple}}{Cy^-\,(aq)} + H^+\,(aq)$$

The colours of CyH and Cy^- are indicated in the above equation.
Acid dissociation constant, K_a, of CyH is 5.0×10^{-5} mol dm^{-3} at 25 °C.

A glass of blackberry juice has a pH of 3.00 at 25 °C. Calculate the ratio of the red to purple form in the juice, and hence predict its colour. [3]

10 An average eggshell weighs about 5 g. Most of the calcium in an eggshell is laid down within a 16h period. This means that it is deposited at a rate of about 125 mg per hour. The calcium required is supplied by special bony masses in the hen's long bones, which accumulate large reserves of calcium for eggshell formation. [The inorganic calcium component of the bone is calcium phosphate, $Ca_3(PO_4)_2$, an insoluble compound.]

The eggshell is largely composed of calcite, a crystalline form of calcium carbonate ($CaCO_3$). Normally, the raw materials, Ca^{2+} and CO_3^{2-}, are carried by the blood to the shell gland. The calcification process is as shown:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$

In the blood, free Ca^{2+} ions are in equilibrium with calcium ions bound to proteins. As the free ions are taken up by the shell gland, more are provided by the dissociation of the protein–bound calcium.

The carbonate ions necessary for eggshell formation are a metabolic by–product. Carbon dioxide produced during metabolism is converted to carbonic acid (H_2CO_3) by the enzyme carbonic anhydrase (CA):

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Carbonic acid ionises stepwise to produce carbonate ions:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

The carbonic acid formed helps to set up a H_2CO_3/HCO_3^- buffer system in the blood plasma of the hen where the pH is maintained at about 7.4. Variation in pH of the blood plasma may alter the structure of important proteins and hence affect certain biological processes.

Chickens do not perspire and so must pant to cool themselves. Panting expels more CO_2 from the chicken's body than normal respiration does.

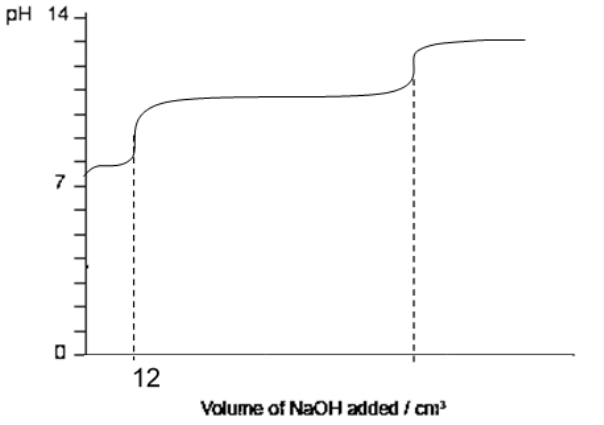
(a) **(i)** Calculate the mass of calcium phosphate required to form one egg.

(ii) Suggest whether eggs produced by the hen on a hot day have thicker or thinner shells when compared to those produced on a cooler day. Explain your answer.

(iii) Write equations to show how the blood plasma of the hen acts as a buffer. [7]

(b) A 10 cm^3 sample of blood plasma was drawn from the hen and titrated against a solution of 7.50×10^{-3} mol dm^{-3} NaOH, using two different indicators, to determine the amount of each of the substances that make up the buffer.

A graph of pH against volume of NaOH was obtained.



(i) Calculate the amount of H_2CO_3 present in the sample of blood plasma.

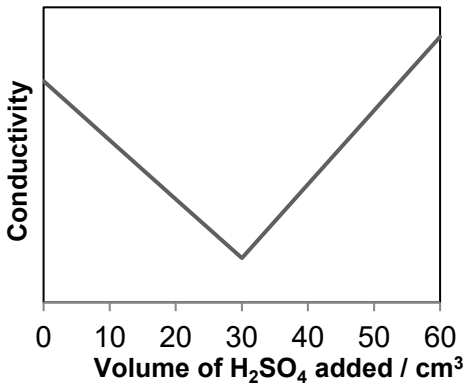
(ii) Calculate the amount of HCO_3^- present in the sample of blood plasma.

(iii) Hence determine the K_a of carbonic acid.

(iv) The theoretical value for the K_a of carbonic acid is 4.47×10^{-7} mol dm^{-3}. Suggest an error or limitation of this experiment which would have resulted in the difference in the value calculated in **(b)(iii).**

(v) Using the theoretical value for the K_a of carbonic acid, calculate the pH of the first endpoint.

11 **(a)** (VJC 2016 P3/Q4) Experiment 1 is conducted in which the conductivity of 25 cm^3 of $Ba(OH)_2$ solution is monitored as it is titrated with 0.10 mol dm^{-3} of aqueous H_2SO_4. The data collected from the experiment is plotted in the graph below.



(i) The conductivity of the $Ba(OH)_2$ solution decreases as the volume of 0.10 mol dm^{-3} H_2SO_4 is added from 0 cm^3 to 30 cm^3.

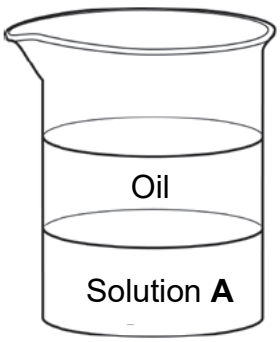
Identify the chemical species that enable the solution to conduct electricity as the first 30 cm^3 of H_2SO_4 (aq) is added. Hence explain why the conductivity decreases. [2]

(ii) Using the information in the graph, calculate the initial concentration of $Ba(OH)_2$. [1]

(b) In Experiment 2, another 25 cm^3 sample of 0.10 mol dm^{-3} aqueous $Ba(OH)_2$ is mixed with 80 cm^3 of 0.10 mol dm^{-3} of ethanoic acid to form solution **A**. Barium ethanoate, $Ba(CH_3CO_2)_2$ is the product of the reaction. The acid dissociation constant, K_a, of ethanoic acid is 1.7×10^{-5} mol dm^{-3}.

Calculate the pH of the solution **A**. [3]

(c) Half of the solution **A** formed in **(b)** is added to beaker **X** where there is a layer of colourless oil as shown in the figure below.



Beaker **X**

The indicator HIn is a weak acid with a pK_a value of 6.0. It reacts with water as represented in the equation below.

$$\underset{\text{yellow}}{HIn(aq)} + H_2O(l) \rightleftharpoons \underset{\text{blue}}{In^-(aq)} + H_3O^+(aq)$$

A small amount of indicator HIn is added into beaker **X**. The mixtures are stirred well and the two layers are allowed to separate.

Assume the pH of solution **A** is unaffected by the presence of colourless oil.

(i) State the colour observed in the oil layer of beaker **X**. Explain the observation in terms of acid–base equilibrium and inter–molecular interactions.

[2]

(ii) A few drops of aqueous sodium hydroxide and hydrochloric acid are added to the beaker **X** successively and stirred well.

Explain with the aid of equation(s) why there is no change in the colour of the oil layer after each addition.

[2]

Answers to Acid–Base Equilibrium

Section A: Multiple Choice Question

1	**D**	**6**	**B**	**11**	**B**	**16**	**D**	**21**	**C**
2	**B**	**7**	**B**	**12**	**C**	**17**	**A**	**22**	**C**
3	**A**	**8**	**C**	**13**	**D**	**18**	**C**		
4	**B**	**9**	**C**	**14**	**C**	**19**	**C**		
5	**D**	**10**	**C**	**15**	**A**	**20**	**B**		

1 There are 3 types of acid and base – *Arrhenius*, *Bronsted–Lowry* and *Lewis* acid/base. The difference among the 3 types of acid/base is in the way the species behaves as an acid/base.

An *Arrhenius* acid or base produces either H^+ or OH^- in a solution respectively. *Lewis* acid or base accepts or donates an electron pair respectively.

Bronsted–Lowry acid is a species which donates a H^+, while a base accepts a H^+ when in solution. In this case, NH_2^- is the 'proton acceptor' and NH_4^+ is the 'proton donor'. Hence, it is classified as *Bronsted–Lowry* acid–base reaction.
Hence, **D is the correct answer.**

The terms 'basic' or 'neutral' or a 'salt' does not explain how the species function as an acid or base and hence is irrelevant in classifying the type of acids.

2 HC*l* is a strong acid, which dissociates completely in water to produce H^+ and Cl^-. HCl is the strongest in the list. Hence, it has the lowest pH.

KC*l* and NH_4Cl are both salts. However, KC*l* is a neutral salt (i.e. pH = 7) but NH_4Cl is an acidic salt (due to NH_4^+ partially dissociating into NH_3 and H^+ in water). Hence NH_4Cl would have a lower pH then KC*l*.

CN^- is the conjugate base of the weak acid, HCN. Hence, CN^- is a weak base compared to KOH. KCN would have a lower pH than KOH.

In order of increasing pH: **HC*l*, NH_4Cl, KC*l*, KCN, KOH**

Answer is **B**.

3 Maximum buffering capacity is when there is equal amount of weak acid/base and its conjugate base/acid. However, 2 species just have to be in large amounts but not necessarily equal in order to make a buffer solution. **A is the incorrect statement.**

A buffer is a species which resist pH changes when a **small amount** of acid or base is added to a solution containing large reservoir of the weak acid/base and large reservoir of its conjugate base/acid. **(D is true.)**

Amino acid, which contains a weak acid group (–COOH) and a weak basic group ($–NH_2$) in the same molecule, can be used to make a buffer by adjusting the pH of the solution. **(B is true.)**

A buffer solution can still act as a buffer *if the slight dilution does not significantly change the concentration of the large reservoir of weak acid/base and its conjugate base/acid , thus* can resist any pH change. **(C is true)**

4 This solution is a NH_3/NH_4^+ buffer and will resist pH increase due to the following reaction:
$NH_3 + H^+ \rightarrow NH_4^+$
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

Addition of small amount of H^+ (2 x 10^{-4} mol) will not change the pH of the solution significantly. pH decreases slightly **(A is false)**. This small amount of H^+ added will be neutralised by the NH_3 present, slightly decreasing $[NH_3]$ **(C is false)** and slightly increasing $[NH_4^+]$ **(B is true and is the answer).**

slightly increasing $[NH_4^+]$, slightly decreasing $[NH_3]$ → ie. molar ratio of NH_4^+ ions to NH_3 molecules in the resulting solution INcreases **(D is false)**.

5 $K_w \propto$ Temperature,
i.e. K_w decreases when temperature decreases (based on data provided)

From the following 3 equations:

Eqn 1: $K_w = [H^+][OH^-]$	$[H^+]$ decrease with decreasing K_w
Eqn 2: $pH = – \lg [H^+]$	pH increases with decreasing $[H^+]$ **(2 is correct)**
Eqn 3: $pK_w = – \lg K_w$	pK_w increases with decreasing K_w **(3 is correct)**

Since $K_b = \frac{[H_3O^+][OH^-]}{[H_2O]}$ and $pK_b = – \lg K_b$,
decreasing K_w would decrease $[OH^-]$ (eqn 1), which in turn increases the pK_b value.
(1 is correct)

Answer is D

6 When temperature increase, K_w increases. This suggest that $[H^+]$ increases resulting in lower pH (see answer for question 5) **(1 is correct)**.

Since $K_w = [H^+][OH^-]$,
$[H^+] = [OH^-] = \sqrt{K_w}$ **(2 is correct)**

$H_2O \rightleftharpoons H^+ + OH^-$

$K_a = \frac{[H_3O^+][OH^-]}{[H_2O]}$

$= \frac{(10^{-7})^2}{55.6} = 1.80 \times 10^{-16} < 1 \times 10^{-14}$

(3 is incorrect)

Answer is B.

7 $pK_a = 10^{-12.6}$ mol dm^{-3}

$[H^+] = \sqrt{Ka \times \frac{1.0 \times 10^{-2}}{0.5}} = \sqrt{10^{-12.6} \times \frac{1.0 \times 10^{-2}}{0.5}} =$ 7.1 x 10^{-8} mol dm^{-3} **(Answer is B)**

8 $[H^+] = [CH_3COO^-] = 10^{-4.4}$ mol dm^{-3}

$K_a = \frac{(10^{-4.4})^2}{(1.3 \times 10^{-4}) - 10^{-4.4}}$ = 1.76 x 10^{-5} **(Answer is C)**

9

$pH = pK_a + \lg \frac{[CH_3COO^-]}{[CH_3COOH]}$

$pK_a = pH - \lg \frac{[CH_3COO^-]}{[CH_3COOH]}$

$= 4.28 - \lg (1/3) = 4.757$

$K_a = 10^{-4.757}$ = 1.75 x 10^{-5} **(Answer is C)**

10

Species	$[H^+]$ (or $[OH^-]$ for NH_3) / mol dm^{-3}	pH	Colour of X	Colour of Y
HCl	0.1 (full dissociation)	1.00	Violet	Yellow
CH_3COOH	See Q7 for full working	2.87	Violet	Yellow
HX	$[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1}$ = 1.34 x 10^{-3} $[H^+] = \sqrt{2.5 \times 10^{-10} \times 0.1}$ = 5.0 x 10^{-6}	5.30	Red	Yellow
NH_3	$[OH^-] = \sqrt{1.8 \times 10^{-5} \times 0.1}$ = 1.34 x 10^{-3}	11.13	Red	Blue

Answer is C.

11 For option **1**, resultant solution contains equal amounts of CH_3COOH and CH_3COO^-. This will certainly give a buffer solution.

For option **2**, HCl will protonate CH_3COO^- to give CH_3COOH. Since there are 2 times more of CH_3COO^- present than HCl added, resultant solution contains equal amount of CH_3COOH and CH_3COO^-. This will certainly give a buffer solution.

For option **3**, each $Mg(CH_3CO_2^-)_2$ provides 2 moles of CH_3COO^-.
Amt of HCl = 2 x amt of $Mg(CH_3CO_2^-)_2$. All CH_3COO^- will be protonated, giving resultant solution with only CH_3COOH. i.e. NOT a buffer solution.

Answer is B.

12 In option **1**, acid–base reaction between HNO_3 and CH_3NH_2 . resultant solution contains excess CH_3NH_2 and $CH_3NH_3^+$ formed from the reaction with HNO_3. A buffer solution will be formed.

In option **2**, acid–base reaction between NaOH and CH_3COOH. resultant solution contains excess NaOH and CH_3COONa. I.e. NOT a buffer solution.

In option **3**, acid–base reaction between HC*l* and NH_3. HC*l* are in equal amounts with NH_3. resultant solution contains NH_4Cl only. I.e. NOT a buffer solution.
Answer is C.

13 $pH = pK_a + \lg \frac{[sodium\ benzoate]}{[benzoic\ acid]}$

$= -\lg (6 \times 10^{-5}) + \lg (\frac{0.1}{0.01}) = 5.22$ **(Answer is D)**

14 New $[NH_3] = \frac{0.1 \times 0.44 - 0.1 \times 0.24}{0.2} = 0.1$ mol dm^{-3}

New $[NH_4^+] = \frac{0.1 \times 0.24}{0.2} = 0.12$ mol dm^{-3}

$pOH = pK_b + \lg \frac{[NH_4^+]}{[NH_3]} = 4.80 + \lg (\frac{0.12}{0.1}) = 4.88$

$pH = 14 - pOH = 9.12$ **(Answer is C)**

15 acid–base reaction between HC*l* with CH_3NH_3. CH_3NH_3 is in excess. resultant solution contains excess CH_3NH_3 and CH_3NH_4Cl. I.e. an alkaline buffer solution.

$HCl + CH_3NH_3 \rightarrow CH_3NH_4Cl$

New $[CH_3NH_3^+] = \frac{0.04 \times 0.1}{0.06} = 0.0667$ mol dm^{-3}

New $[CH_3NH_2] = \frac{0.02 \times 0.30 - 0.04 \times 0.10}{0.06} = 0.0333$ mol dm^{-3}

$pOH = 14 - pH = 14 - 10.5 = 3.50$

$pOH = pK_b + \lg (\frac{[CH_3NH_3^+]}{[CH_3NH_2]})$

$pK_b = pOH - \lg (\frac{[CH_3NH_3^+]}{[CH_3NH_2]})$

$= 3.50 - \lg (\frac{0.0667}{0.0333}) = 3.20$ **(Answer is A)**

16 Adding HC*l* to HCO_3^- forms H_2CO_3. Using excess amount of HCO_3^-, we can get a solution containing a large reservoir of both HCO_3^- and H_2CO_3 , thus forming a buffer solution **(A is true).**

$pH = pK_a + \lg (\frac{[HCO_3^-]}{[H_2CO_3]})$

lg $\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$ = pH – p*K*a = 7.4 – [–lg (7.90 x 10^{-7})] = 1.30

$\frac{[HCO_3^-]}{[H_2CO_3]}$ = $10^{-1.3}$ = 0.05 (ie. 1/20) **(B is true)**

Dilution changes the concentration of both HCO_3^- and H_2CO_3 to the same extent, hence the ratio of the amount of both species present remains high, allowing it to behave as a buffer resisting any pH changes **(C is true)**.

Since the ratio of HCO_3^- to H_2CO_3 is not 1:1, the buffer is not at its maximum buffering capacity. pH ≠ pK_a **(D is false and is the answer)**

17 When 12.5 cm^3 of CH_3NH_2 is added, HCl is still in excess. The pH of the resulting solution is the pH of the excess HCl solution. The new total volume is 37.5 cm^3. $CH_3NH_3^+$ being a weak acid, would be suppressed from dissociating in the presence of a strong acid.

pH = – lg $\left(\frac{0.0125 \times 0.1}{0.0375}\right)$ = 1.48 **(Answer is A)**

18 The initial pH is 1 with no buffering region. This indicates a strong acid was originally in the conical flask.

Equivalence point occurs at pH <7. Ie. Acidic salt formed. Strong acid reacts with weak base to give acidic salt.

25 cm^3 of weak base is required to reach equivalence point with 25 cm^3 of an acid. This suggest that the stoichiometry ratio of H^+ : base is 1:1.

(answer is C)

19 Equivalence point occurs at pH >7. Ie. basic salt formed (between strong base NaOH and weak acid).

The titration has a final pH of close to 3. This confirms a weak acid is added into the strong NaOH base **(B is incorrect)**.

10 cm^3 of 0.10 mol dm^{-3} weak acid is needed to reach equivalence point with 10 cm^3 of 0.10 mol dm^{-3} NaOH. This suggest that the weak acid is a monobasic acid **(D is wrong)**.

Since the maximum buffering region is after the equivalence point, maximum buffering region is at twice the volume needed to reach equivalence point (20cm^3 in this case – point **J**).

(C is answer)

20 When HNO_3 is added Na_2CO_3, HCO_3^- and H_2CO_3 are formed.
$HNO_3 + Na_2CO_3 \rightarrow NaHCO_3 + NaNO_3$ (1st equivalence point, phenolphthalein)
$HNO_3 + NaHCO_3 \rightarrow H_2CO_3 + NaNO_3$ (2nd equivalence point, methyl orange)

As H_2CO_3 is a dibasic weak acid, there will be 2 buffering regions that result.
20.0 cm^3 of HNO_3 is needed to convert the CO_3^{2-} into HCO_3^- (1st equivalence point), and another 20.0 cm^3 of HNO_3 to convert HCO_3^- to H_2CO_3 (2nd equivalence point).

B is the correct answer with 2 buffering regions and equivalence points at the correct volume of HNO_3 added.

21 1st equivalence point: $H_2C_2O_4 + NaOH \rightarrow NaHC_2O_4 + H_2O$
2nd equivalence point: $NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$

Methyl orange can be used to determine the amount of NaOH needed for the complete conversion of $H_2C_2O_4$ into $HC_2O_4^-$. This, in turn, can be used to find the amount and concentration of $H_2C_2O_4$ present **(A is incorrect)**.

20 cm^3 of NaOH is needed to completely react with the $H_2C_2O_4$ present. This indicates (0.20 x 0.02) ÷ 2 = 0.002 mol of $H_2C_2O_4$ is present in the solution. This means that 0.002 ÷ 0.1 = 0.02 dm^3 (or 20 cm^3) of 0.10 mol dm^{-3} of $H_2C_2O_4$ is present **(B is incorrect)**.

When 20 cm^3 of NaOH is added, all the weak $H_2C_2O_4$ acid are reacted away, giving a conjugate base, $C_2O_4^{2-}$. At this point, $C_2O_4^{2-}$ undergo hydrolysis to give OH^-, according to the equation: $C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$. There should be more OH^- than H^+ **(D is incorrect)**.

Point A indicates the 2nd maximum buffering region (for eqm 2). At this region, there is equal amount of $HC_2O_4^-$ and $C_2O_4^{2-}$ **(C is correct)**.

22 1st equivalence point: $H_3N^+CH(CH_3)COOH + OH^- \rightarrow H_3N^+CH(CH_3)COO^- + H_2O$
2nd equivalence point: $H_3N^+CH(CH_3)COO^- + OH^- \rightarrow H_2NCH(CH_3)COO^- + H_2O$

At pH = pK_1, solution is at its maximum buffering capacity. Hence, there is an equal $H_3N^+CH(CH_3)COOH$ and $H_3N^+CH(CH_3)COO^-$ **(option 2 is correct)**.

At pH = 7, solution is at its first equivalence point (point where the slope of the curve is at a maximum). All $H_3N^+CH(CH_3)COOH$ will be reacted to produce $H_3N^+CH(CH_3)COO^-$, not $H_2NCH(CH_3)CO_2^-$ **(option 1 is incorrect)**.

$H_3N^+CH(CH_3)COO^-$ has no net charge **(option 3 is correct)**.

Answer is **C**.

Section B: Structured Question

1 (i) $K_a = \dfrac{[CH_3CH(OH)COO^-][H^+]}{[CH_3CH(OH)COOH]}$

(ii) No. of moles of lactic acid = 0.20/90.0 = 2.22×10^{-3} mol
volume of NaOH required = $(2.22 \times 10^{-3}) \div 0.10 \times 1000 = 22.2$ cm^3

(iii) No. of moles of $CH_3CH(OH)CO_2^-$ salt formed at equivalence point
= 2.22×10^{-3} mol

$[CH_3CH(OH)CO_2^-] = 22 \times 10^{-3} \div \frac{22.2+20.0}{1000}$
= 0.0526 mol dm^{-3}

K_b of $CH_3CH(OH)CO_2^-$ = $\frac{Kw}{Ka} = \frac{1\times 10^{-14}}{1.38 \times 10^{-4}}$ = 7.25 x 10^{-11} mol dm^{-3}

$[OH^-] = \sqrt{K_b \times [CH_3CH(OH)CO_2^-]} = \sqrt{7.25 \times 10^{-11} \times 0.0526}$
=1.95 x 10^{-6} mol dm^{-3}
pOH = 5.71
pH = 14 – 5.71 = **8.29**

(iv) Cresol red because the pH at the equivalence point is within the working range of the indicator. (equivalence pH = 8.29).

2 (a) A weak Bronsted base is a **proton acceptor** that **dissociates partially** in solution.

(b)(i) Methyl orange is a suitable indicator. Its working range (pH 3.2 – 4.2) lies **within** the range of **rapid** pH change of the titration. (Acidic salt formed between HCl and TIPA a weak base, hence equivalence point will occur at pH <7.)

(ii) [**TIPA**] =(25.00 x 0.05) / 20.0 = 0.0625 mol dm^{-3}

(iii) Max buffer capacity occurs when V_{HCl} added = 12.50 cm^3
pK_b = pOH = 14 – 9.6 = 4.4
K_b = $10^{-4.4}$ = 3.98 x 10^{-5} mol dm^{-3}

(iv) K_b = 3.98 x 10^{-5} mol dm^{-3}
$[OH^-] = \sqrt{3.98 \times 10^{-5} \times 0.0625}$
= 1.577 x 10^{-3} mol dm^{-3}
pH = 14 – [–lg(1.577 x 10^{-3})]
= 11.2

(c)(i) $N(C_3H_6OH)_3 + HNO_3 \rightarrow NH(C_3H_6OH)_3^+NO_3^-$
(Similiar to $NH_3 + HNO_3 \rightarrow NH_4^+NO_3^-$)

(ii) The product is $NH(C_3H_6OH)_3^+NO_3^-$, which has a **giant ionic structure**. **TIPA** has a **simple molecular structure**.

A lot of energy is required to break the **strong ionic bonds** between $NH(C_3H_6OH)_3^+$ and NO_3^- ions, giving it a high melting point. Little energy is required to break the **weaker hydrogen bonding** between **TIPA** molecules.

(d)(i) $K_{sp} = [Mg^{2+}][OH^-]^2 = 0.0717 \times [10^{-(14-8.7)}]^2$
$= 1.80 \times 10^{-12}$ mol^3 dm^{-9}

(ii) $K_{sp} = [Mg^{2+}][OH^-]^2$
$1.80 \times 10^{-12} = [Mg^{2+}]\,[10^{-(14-12)}]^2$
$[Mg^{2+}] = 1.80 \times 10^{-8}$ mol dm^{-3}

(iii) Since $[Mg^{2+}]_{\text{second sample}} << [Mg^{2+}]_{\text{first sample}}$,
the first soil sample would favour a good cultivation of rice crop.
(Question stated in "magnesium ion deficiency in the soil decreases the grain quality and protein content of the rice crop cultivated.")

(iv) $NH(C_3H_6OH)_3^+$ present in $NH(C_3H_6OH)_3^+NO_3^-$ is **acidic** *[or undergoes **hydrolysis** or $NH(C_3H_6OH)_3^+ + H_2O \rightleftharpoons N(C_3H_6OH)_3 + H_3O^+$]*.

The H_3O^+ produced helps to **dissolve** the insoluble $Mg(OH)_2$ via neutralisation.

3 (i) Hydrazine has an available lone pair of electrons on the N–atom, hence able to accept protons.

(ii)
$$K_b = \frac{[OH^-][N_2H_5^+]}{[N_2H_4]}$$

(iii)
$$K_b = \frac{10^{-14}}{3.33 \times 10^{-9}} = 3.003 \times 10^{-6} \text{ mol dm}^{-3}$$

$$K_b = 3.00 \times 10^{-6} = \frac{[OH^-][N_2H_5^+]}{[N_2H_4]}$$

$[OH^-] = \sqrt{3.003 \times 10^{-6} \times 0.2} = 7.749 \times 10^{-4}$ mol dm^{-3}

pOH = 3.11
pH = 10.9

4 (a) $pH = pK_a + \lg [C_5H_7O_4CO_2Na]/[C_5H_7O_4CO_2H]$

$[C_5H_7O_4CO_2Na] = \frac{2.48}{198} \div \frac{25}{1000} = 0.5010$ mol dm^{-3}

$pH = -\lg (7.40 \times 10^{-4}) + \lg \frac{0.5010}{0.200}$
$= 3.53$

(b) Since pH is raised on addition of the solid, the solid added must be a base.
$C_5H_7O_4CO_2H + OH^- \rightarrow C_5H_7O_4CO_2^- + H_2O$
$3.73 = -\lg (7.40 \times 10^{-4}) + \lg [C_5H_7O_4CO_2Na]/[C_5H_7O_4CO_2H]$
$[C_5H_7O_4CO_2Na]/[C_5H_7O_4CO_2H] = 3.97$

Let the molar mass of the solid be **M**
$n_{citric\ acid} = 0.025 \times 0.200 - 0.059/\mathbf{M}$
$n_{citrate} = 2.48/198 + 0.059/\mathbf{M}$
$\frac{2.48/198+0.059/M}{0.025\times0.200-0.059/M} = 3.97 \quad \therefore \mathbf{M} = 40.0$

Solid is sodium hydroxide.

(c) pH at max. buffering capacity = 3.13
$C_5H_7O_4CO_2^- + H_3O^+ \rightarrow C_5H_7O_4CO_2H + H_2O$

Let the volume of 0.100 mol dm^{-3} HCl required be **V,**
$n_{citric\ acid} = 0.025 \times 0.200 + 0.100\mathbf{V}$
$n_{citrate} = 2.48/198 - 0.100\mathbf{V}$

At max. buffering capacity,

$[C_5H_7O_4CO_2H] = [C_5H_7O_4CO_2^-]$
$\therefore n_{citric\ acid} = n_{citrate}$

$0.025 \times 0.200 + 0.100\mathbf{V} = 2.48/198 - 0.100\mathbf{V}$
$\mathbf{V} = 0.0376\ dm^3 = 37.6\ cm^3$

5 (i) $HCO_3^- + H^+ \rightarrow H_2CO_3$
large reservoir of HCO_3^- neutralises small amount of H^+ added, hence concentration of H^+ remains almost constant

$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$
large reservoir of H_2CO_3 neutralises small amount of OH^- added, hence concentration of OH^- remains almost constant

Hence pH is maintained.

(ii) $pK_a = 6.10$
$K_a = 7.94 \times 10^{-7}$ mol dm^{-3}

$K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 7.94 \times 10^{-7}$

Since pH = 7.4, $[H^+]$ = 3.981 x 10^{-8} mol dm^{-3}

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 19.95 \text{ (or 20:1)}$$

(iii)

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 19.95$$

$[HCO_3^-]$ = 19.95 x 0.05 = 0.9975 mol dm^{-3}

No. of moles of HCO_3^- = 0.9975 x 2.0 = 1.995 mol (or $[HCO_3^-]_{new}$)

No. of moles of H_2CO_3 = 0.05 x 2.0 = 0.100 mol (or $[H_2CO_3]_{new}$)

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 7.94 \times 10^{-7}$$

$$\frac{[H^+](1.995 - 0.03)/2.0}{(0.100 + 0.03)/2.0} = 7.94 \times 10^{-7}$$

$[H^+]$ = 5.253 x 10^{-8} mol dm^{-3}

New pH = 7.28

6 (a) 8.8 (allow any value from 8.4 to 9.0)

Reason: Low [HA], thus small addition of OH^- has great effect / OH^- increases rapidly as NaOH is a strong base / logarithmic nature of pH;

(b) volume of NaOH for complete neutralisation = 8.1 cm^3 (*exact*)
amount of NaOH = 8.1 / 1000 × 0.1 = 0.00081 mol = amt of HA in 10 cm^3
[HA] = 0.00081 / 0.010 = 0.081 mol dm^{-3}

(c) correct pH reading from graph(2.9)(*allow 2.8 or 3.0)*

Thus $[H^+]$ = 1.258 ×10^{-3} mol dm^{-3}

$K_a = \frac{(1.258\times10^{-3})^2}{0.081-1.258\times10^{-3}}$ = 1.984 × 10^{-5} mol dm^{-3};

pK_a = 4.70 (***Accept 4.7 and allow ECF).*

7 (a)(i)

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}$$

No. of moles of NaOH used = $\frac{30}{1000}$ x 0.45 = 0.0135

No. of moles of CH_3CO_2H = No. of moles of NaOH used = 0.0135

$[CH_3CO_2H]$ in vinegar sample = $\frac{0.0135}{25/1000}$ = 0.540 mol dm^{-3}

pH of vinegar sample = 2.50 , $[H^+] = 10^{-2.5} = 3.162 \times 10^{-3}$ mol dm^{-3}

$K_a = \frac{(3.162\times10^{-3})^2}{0.540-3.162\times10^{-3}}$

= **1.86 x 10^{-5} mol dm^{-3} (shown)**

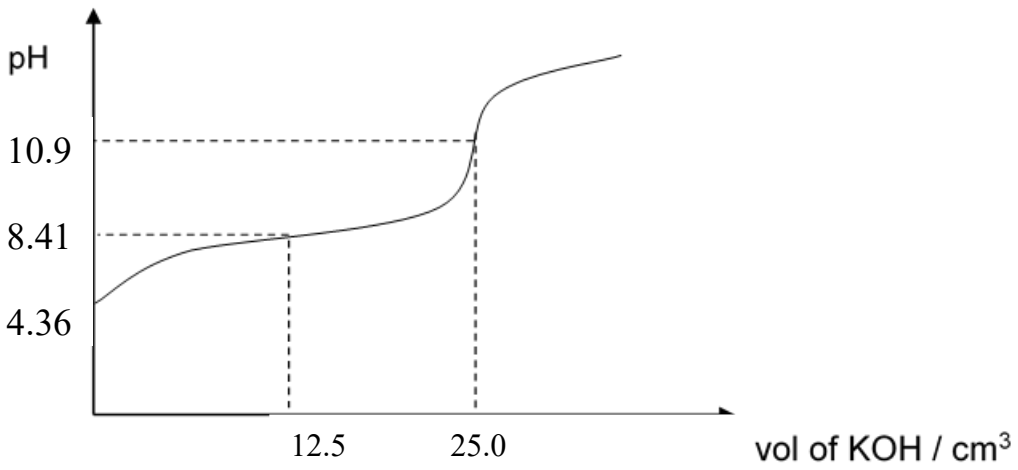
(assume that the degree of dissociation of CH_3CO_2H < 0.540 mol dm^{-3})

(ii) Indicator: **Phenolphthalein or thymolphthalein**

Reason for choice:
The titration between a weak acid and strong base will produce a basic salt (pH > 7) at equivalence point. The working range of the indicator (around 8.0 – 10) **lies within the sharp pH change** over the equivalence point.

8 (i) Let Coc be cocaine.
Hence Cocaine hydrochloride is CocHC*l*
When cocaine hydrochloride was titrated with aqueous KOH,
CocHC*l* + KOH → Coc + KC*l* + H_2O
At equivalence point, Coc, KC*l* and H_2O is present.
Only Coc affects pH as cocaine undergoes hydrolysis:
Coc + H_2O ⇌ $CocH^+ + OH^-$
$K_b = 10^{-5.59} = 2.57 \times 10^{-6}$ mol dm^{-3}
$[OH^-] = \sqrt{2.57 \times 10^{-6} \times 0.25} = 8.016 \times 10^{-4}$ mol dm^{-3}
pOH = 3.10
pH = 10.9

(ii)



*Question asked for "Mark clearly on your sketch the pH values at **maximum buffering capacity** and **at the equivalence point**."*

*pH value at **maximum buffering capacity***

For an alkaline buffer, $pOH = pKb + \lg \frac{[Salt]}{[weak\ base]}$

$pOH = pK_b = 5.59$

$pH = 14 - 5.59 = 8.41$

Initial pH of cocaine hydrochloride, BH^+Cl^-

$BH^+ \rightleftharpoons B + H^+$

$K_a = \frac{[B][H+]}{[BH^+]}$

$[H^+] = \sqrt{10^{-8.41} \times 0.5} = 4.41 \times 10^{-5}$ mol dm^{-3}

pH = 4.36

(iii) The sharp change of pH at the equivalence point falls outside the working range of methyl orange.

9 (a) (i) pH = 12.5
pOH = 14 – 12.5 = 1.5
$[OH–] = 10^{-1.5} = 0.0316$ mol dm^{-3} [**1**]

MOH has dissociated completely, thus it is a strong base [**1**].

(ii) $CH_3CH_2COOH + MOH \rightarrow CH_3CH_2COO^-M^+ + H_2O$

Amt of MOH = 0.031 x 25/1000
= 7.75 x 10^{-4} mol

Amt of CH_3CH_2COOH required = 7.75 x 10^{-4} mol [**1**]

Volume of CH_3CH_2COOH required = (7.75 x 10^{-4}) / 0.025
= 0.031 dm^3
= 31.0 cm^3

V = 31.0 [**1**]

(iii) When V cm^3 of acid is added, the acid and base react completely to produce a **basic salt**, which undergoes **hydrolysis** in water to **produce hydroxide ions / an alkaline solution**. [1]

$CH_3CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(aq) + OH^-(aq)$ [1]

(b) When a mix of CyH and Cy– is present, system is an acidic buffer.

$$\mathbf{pH = pK_a + \lg \frac{[salt]}{[acid]}}$$

$$3.00 = -\lg (5.0 \times 10^{-5}) + \lg \frac{[\mathbf{Cy^-}]}{[\mathbf{CyH}]} \quad [\mathbf{1}]$$

$$\frac{[\mathbf{Cy^-}]}{[\mathbf{CyH}]} = 0.05$$

$$\frac{[\mathbf{CyH}]}{[\mathbf{Cy^-}]} = 20 : 1 \quad [\mathbf{1}]$$

Colour of juice: red [**1**]

10 (a)(i) $Ca_3(PO_4)_2 \rightarrow 3Ca + 2P + 8O$

Amount of calcium required = $\frac{125 \times 16}{1000} \div 40.1$

= 0.04988 mol

Mass of calcium phosphate required

= $\frac{0.04988}{3}$ x [3 x 40.1 x 2(31.0 + 4 x 16.0)]

= 5.16 g

(ii) On a hot day, chickens pant to cool themselves and hence expel CO_2, i.e. amount of CO_2 in blood decreases.

This causes the position of the equilibrium of all above reaction systems to shift to the left so as to compensate of the excessive loss of CO_2 in blood. This decreases the $[CO_3^{2-}]$ in the blood and hence the formation of $CaCO_3$, resulting in thinner eggshells.

(iii) $H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$ / $HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O(l)$

(b)(i) At the first endpoint, ***$H_2CO_3(aq) + NaOH(aq) \rightarrow NaHCO_3(aq) + H_2O(l)$***

Amount of H_2CO_3 present = Amount of NaOH used for the 1st Endpoint

= $\frac{1.30}{1000}$ x 7.50 x 10^{-3} = 9.75 x 10^{-6} mol

(ii) At the second endpoint, **$NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$**

Amount of HCO_3^- present for step 2 of the titration

= Amount of HCO_3^- present originally + Amount of HCO_3^- produced from step 1 of the titration

= Amount of HCO_3^- present originally + 9.75 x 10^{-6}

Amount of HCO_3^- present altogether

= Amount of NaOH used for the 2nd endpoint only

= $\frac{14.60}{1000}$ x 7.50 x 10^{-3}

= 1.095 x 10^{-4} mol

Amount of HCO_3^- present originally = $1.095 \times 10^{-4} - 9.75 \times 10^{-6}$ mol
= 9.98×10^{-5} mol

(iii)

$$\text{pH of buffer} = pK_a + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$7.4 = pK_a + \lg \frac{\left(9.975 \times 10^{-5} / 10.0\right)}{\left(9.75 \times 10^{-6} / 10.0\right)}$$

$$pK_a = 7.4 - \lg\left(\frac{9.975 \times 10^{-5}}{9.75 \times 10^{-6}}\right)$$

$$pK_a = 6.39$$

$$K_a = 4.07 \times 10^{-7} \text{ mol dm}^{-3}$$

(iv) There is a large percentage error in the titration values recorded as the volume of NaOH used for the first endpoint is very small. OR

$$\% \text{ error} = \frac{uncertainty\ of\ burette\ reading}{volume} \times 100$$

$$= \frac{2 \times 0.05}{1.30} \times 100 = 7.69\%$$

(v) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

$$K_w = K_a \times K_b$$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{4.47 \times 10^{-7}}$$

$$= 2.237 \times 10^{-8} \text{ mol dm}^{-3}$$

(v)

$$[HCO_3^-] = 9.975 \times 10^{-5} \div \frac{11.30}{1000} = 8.827 \times 10^{-3}\,\text{moldm}^{-3}$$

$$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$$

$$K_b = \frac{[OH^-]^2}{[HCO_3^-]}$$

$$2.237 \times 10^{-8} = \frac{[OH^-]^2}{[8.827 \text{ x } 10^{-3}]}$$

$$[OH^-] = 1.405 \times 10^{-3}\,\text{moldm}^{-3}$$

pH = 14 – pOH = 9.15

11 (a) (i) Species: $Ba^{2+}(aq)$ and $OH^-(aq)$

As the titration proceeds before the equivalence point,
$OH^-(aq)$ is removed by neutralisation to form $H_2O(l)$.
$Ba^{2+}(aq)$ is removed by precipitation to form $BaSO_4(s)$.
Thus there are less ions to act as mobile charge carriers, and conductivity decreases.

(ii) $Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$

$n_{Ba(OH)_2} = n_{H_2SO_4}$

No. of moles of $Ba(OH)_2$ = 30/1000 × 0.10 = 0.003 mol

Concentration of $Ba(OH)_2$ = 0.003 / 0.025 = 0.12 mol dm^{-3}

(b) $Ba(OH)_2$ is the limiting reagent.

Resultant solution contains $Ba(CH_3CO_2)_2$ and CH_3CO_2H, i.e. acidic buffer. $Ba(OH)_2 + 2CH_3CO_2H \rightarrow Ba(CH_3CO_2)_2 + 2H_2O$

Amt of $Ba(OH)_2$ reacted = $\frac{25}{1000}$x 0.10 = amt of $Ba(CH_3CO_2)_2$ formed.

amt of $CH_3CO_2^-$ formed= $\frac{25}{1000}$x 0.10 x 2 mol

New $[CH_3CO_2^-]$ = 2 x $\frac{25}{1000}$ x 0.10 ÷ $\frac{105}{1000}$

= 0.0476 mol dm^{-3}

Amt of CH_3CO_2H unreacted = $\frac{80-50}{1000}$ x 0.10

New $[CH_3CO_2H] = \frac{80-50}{1000} \times 0.10 \div \frac{105}{1000} = 0.0286$ mol dm^{-3}

$$\textbf{pH} = \textbf{p}K_a + \textbf{lg}\ \frac{[\textbf{salt}]}{[\textbf{acid}]}$$

$$= -\ \textbf{lg}\ (1.7 \times 10^{-5}) + \textbf{lg}\ \frac{[CH_3COO^-]}{[CH_3COOH\ \ ]} \quad [\textbf{1}]$$

$$= -\ \textbf{lg}\ (1.7 \times 10^{-5}) + \textbf{lg}\ \frac{0.0476}{0.0286}$$

$$= \textbf{4.99}$$

OR $K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH\ \ ]}$

$$1.7 \times 10^{-5} = \frac{[H^+]0.0476}{0.0286}$$

$[H^+] = 1.02 \times 10^{-5}$ mol dm^{-3}

pH = –lg (1.02×10^{-5})
= **4.99**

(i) The oil layer is yellow in colour.

Solution **A** is of pH 4.99, acid form of indicator HIn(aq) predominates since pH < pK_a.

Since HIn is a neutral (uncharged) molecule, some of it can dissolve better in the oil layer because of tdid interactions with the oil molecules.

(ii) On addition of NaOH, large reservoir of CH_3CO_2H removes the small amount of OH^- added.

$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$
On addition of HC*l*, large reservoir of $CH_3CO_2^-$ removes the small amount of H^+ added.

$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$

$[H^+]$ remains unchanged, the HIn form still predominates and is soluble in the oil layer.

3. SOLUBILITY EQUILIBRIUM

Section A: Multiple Choice Question

1 Magnesium arsenate, $Mg_3(AsO_4)_2$, is a sparingly soluble salt commonly used to make insecticides. It dissociates in water according to the equation below.

$$Mg_3(AsO_4)_2\,(s) \rightleftharpoons 3\,Mg^{2+}\,(aq) + 2\,AsO_4^{3-}\,(aq)$$

If the solubility product is S, what is the value of $[AsO_4^{3-}\,(aq)]$ at equilibrium?

A $S^{1/5}$

B $(\frac{2}{3}S)^{1/5}$

C $(\frac{2}{5}S)^{1/5}$

D $(\frac{8}{27}S)^{1/5}$

2 The numerical values of the solubility product of $BaSO_4$, $BaCO_3$ and $Ba(IO_3)_2$ at 25 °C are given in the table below.

Compound	Solubility product
$BaSO_4$	1.1×10^{-10}
$BaCO_3$	2.6×10^{-9}
$Ba(IO_3)_2$	4.0×10^{-9}

An aqueous solution of $BaCl_2$ was added slowly, until in excess, to a solution containing 0.5 mol dm^{-3} Na_2SO_4, 1.0 mol dm^{-3} Na_2CO_3 and 1.5 mol dm^{-3} $NaIO_3$ at 25 °C.

What is the correct order of precipitation of the three barium salts?

	First to precipitate ⟶		Last to precipitate
A	$BaSO_4$	$BaCO_3$	$Ba(IO_3)_2$
B	$Ba(IO_3)_2$	$BaCO_3$	$BaSO_4$
C	$BaSO_4$	$Ba(IO_3)_2$	$BaCO_3$
D	$BaCO_3$	$Ba(IO_3)_2$	$BaSO_4$

3 Solid calcium hypochlorite pellets, $Ca(ClO)_2(s)$, are added to swimming pools to form HC*l*O(aq), which kills disease–causing bacteria and algae.

$$Ca(ClO)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2ClO^-(aq)$$

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

What is the effect on the solubility of calcium hypochlorite and bacterial growth when pH decreases?

	Solubility of calcium hypochlorite	effect on bacterial growth
A	decreases	more favourable
B	decreases	less favourable
C	increases	more favourable
D	increases	less favourable

4 A sparingly soluble salt, $Mg_3(PO_4)_2$ dissociates in aqueous solution as follows:

$$Mg_3(PO_4)_2 \rightleftharpoons 3\ Mg^{2+} + 2\ PO_4^{3-}$$

Given that the solubility product, K_{sp} of $Mg_3(PO_4)_2$ is ***Q***, what is the value of $[Mg^{2+}]$ in a saturated solution?

A $(\frac{9Q}{4})^{\frac{1}{5}}$

B $(\frac{Q}{27})^{\frac{1}{3}}$

C $(\frac{Q}{108})^{\frac{1}{5}}$

D $(\frac{9Q}{64})^{\frac{1}{3}}$

5 The concentration of Sr^{2+} ions in a 0.5 dm^3 solution is 2.0×10^{-2} mol dm^{-3}. Na_2CO_3 solid was added to the solution in excess until the concentration of CO_3^{2-} ions remained at 2.5×10^{-6} mol dm^{-3}.

Given that the K_{sp} of $SrCO_3$ is 1.6×10^{-9}, what mass of $SrCO_3$ was precipitated?

A 0.0472 g

B 0.0944 g

C 1.43 g

D 2.86 g

6 The K_{sp} values of three metal hydroxides are given in the table below.

metal hydroxide	K_{sp}
$Ca(OH)_2$	4.7×10^{-6} mol^3 dm^{-9}
$Sn(OH)_2$	5.4×10^{-27} mol^3 dm^{-9}
$Cr(OH)_3$	6.7×10^{-31} mol^4 dm^{-12}

Which statements are correct?

1 The concentration of OH^- in a saturated solution of $Ca(OH)_2$ is 0.021 mol dm^{-3}.

2 $Ca(OH)_2(s)$ will be precipitated if equal volumes of 0.02 mol dm^{-3} NaOH(aq) and 0.02 mol dm^{-3} $Ca(NO_3)_2(aq)$ are mixed together.

3 $Cr(OH)_3$ has the lowest solubility amongst the three metal hydroxides.

A 1, 2 and 3 are correct **B** 1 and 2 are correct **C** 2 and 3 are correct **D** 1 only is correct'

7 Which statement explains the observations that magnesium hydroxide dissolves in ammonium chloride, but not in aqueous sodium chloride?

A The ammonium ion changes the solubility product of $Mg(OH)_2$.

B NH_4^+ ion is first formed, and then acts through a common ion effect.

C NH_4Cl dissociates less fully than NaCl.

D The NH_4^+ ion acts as an acid.

8 A saturated solution of $Ca(OH)_2$ is found to have a pH of 12.3 at 25 °C.
Which statement is **incorrect**?

A The K_{sp} of $Ca(OH)_2$ is 4×10^{-6} mol^3 dm^{-9}.
B The solubility of $Ca(OH)_2$ would increase when temperature is raised to 35 °C.
C The solubility of $Ca(OH)_2$ will decrease when solid Na_2O is added.
D The pH of the solution would increase when $Ca(NO_3)_2$ is added

9 The yellow pigment used for road markings is lead(II) chromate, $PbCrO_4$.
Concentrated lead(II) nitrate is added dropwise to 0.010 mol dm^{-3} potassium chromate(IV).
What is the concentration of lead(II) ions when the first trace of precipitate appears?
(K_{sp} of $PbCrO_4$ = 1.69 x 10^{-14} mol^2 dm^{-6})

A 1.69×10^{-14} mol dm^{-3}
B 1.69×10^{-12} mol dm^{-3}
C 1.30×10^{-9} mol dm^{-3}
D 1.30×10^{-7} mol dm^{-3}

10 Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the primary mineral in tooth enamel. Dental cavities are caused when acids dissolve tooth enamel.

$$Ca_{10}(PO_4)_6(OH)_2(s) + 8H^+(aq) \rightleftharpoons 10Ca^{2+}(aq) + 6HPO_4^{2-}(aq) + 2H_2O(l)$$

Which of the following statements are correct?

1 Acids produced from food debris on the tooth surface speeds up tooth decay.
2 Dental cavities are formed more readily when the saliva is more acidic.
3 Fluoride used in dental treatment replaces OH^- in hydroxyapatite with F^- and thus helps to slow down tooth decay.

A 1, 2 and 3 are correct **B** 1 and 2 are correct **C** 2 and 3 are correct **D** 1 only is correct

11 The solubility of $Pb(OH)_2$ in water at 25°C is 1.06×10^{-5} mol dm^{-3}.

What is the solubility of $Pb(OH)_2$ in a buffer solution of pH 12.8 at the same temperature?

A 1.06×10^{-5} mol dm^{-3}
B 1.06×10^{-8} mol dm^{-3}
C 1.19×10^{-12} mol dm^{-3}
D 1.19×10^{-15} mol dm^{-3}

12 The numerical values of the solubility products at 25 °C for AgC*l* and AgI are 1.6×10^{-10} and 8.0×10^{-17} respectively.
What is the equilibrium constant for the reaction below?

$$AgCl(s) + I^-(aq) \rightleftharpoons AgI(s) + Cl^-(aq)$$

A 1.3×10^{-26}

B 5.0×10^{-7}

C 1400

D 2.0×10^{6}

13 A solution contains 1×10^{-3} mol dm^{-3} of bromide, fluoride, iodide and sulfate ions.
Which lead(II) compound will be precipitated first when 0.01 mol dm^{-3} of lead(II) nitrate is added dropwise into the solution?

	compound	numerical value of solubility product (at 25°C)
A	Lead(II) bromide	4.0×10^{-5}
B	Lead(II) fluoride	2.7×10^{-8}
C	Lead(II) iodide	7.1×10^{-9}
D	Lead(II) sulfate	1.6×10^{-8}

14 Value of solubility product, K_{sp}, of silver ethanedioate, $Ag_2C_2O_4$, at 298K is 6.10×10^{-12}.
What is the concentration of Ag^+ in a saturated solution of $Ag_2C_2O_4$ at 298 K?

A 1.23×10^{-6} mol dm^{-3}

B 2.47×10^{-6} mol dm^{-3}

C 1.15×10^{-4} mol dm^{-3}

D 2.30×10^{-4} mol dm^{-3}

15 In an experiment, 1.00×10^{-2} mol of silver nitrate, $AgNO_3$, and 9.00×10^{-3} mol of calcium nitrate, $Ca(NO_3)_2$, are dissolved in a solution containing 0.100 mol dm^{-3} of sulfuric acid, H_2SO_4.
The solubility product of Ag_2SO_4 is 1.20×10^{-5} mol^3 dm^{-9} and that of $CaSO_4$, is 7.10×10^{-5} mol^2 dm^{-6}.
Which statement is correct?

A No precipitate is formed.

B Only $CaSO_4$ is precipitated.

C $CaSO_4$ is precipitated followed by Ag_2SO_4.

D Ag_2SO_4 is precipitated followed by $CaSO_4$.

16 The numerical values of the solubility product of calcium carbonate and calcium fluoride at 25 °C are 8.7 x 10^{-9} and 4.0 x 10^{-11} respectively.

Which statement is correct?

A Calcium carbonate has a higher solubility than calcium fluoride.

B Addition of sodium fluoride to a saturated solution of calcium fluoride increases the ionic product of calcium fluoride.

C Addition of sodium carbonate to a solution containing calcium carbonate decreases the solubility product of calcium carbonate.

D Addition of calcium nitrate to a solution containing 1 mol dm^{-3} each of carbonate and fluoride ions causes calcium carbonate to precipitate out first.

Section B: Structured Question

1 This question refers to compounds of calcium and barium.

Oil paints contain traces of red Ca^{2+} and green Ba^{2+} ions which give them their characteristic red and green colours respectively. Oil painting is typically done on canvas. During the manufacturing process of canvas, hydrogen orthoperiodate ions, HIO_6^{4-}, is left on the canvas.

Orthoperiodate salts are formed when orthoperiodate ions, IO_6^{5-}, reacts with the Ca^{2+} and Ba^{2+} ions in the paint, causing the decolourisation of the red and green colour of the paint. The equations below show the formation of IO_6^{5-} and its salts.

$HIO_6^{4-}(aq) \rightleftharpoons H^+(aq) + IO_6^{5-}(aq)$ $\quad K_a = 4.04 \times 10^{-6}$ mol dm^{-3}

$5\ M^{2+}(aq) + 2\ IO_6^{5-}(aq) \rightarrow M_5(IO_6)_2(s)$ $\quad$ where M^{2+} is Ca^{2+} or Ba^{2+}

Relevant K_{sp} values are given in the table below :

Salt	K_{sp}
$Ca_5(IO_6)_2$	4.0 x 10^{-9}
$Ba_5(IO_6)_2$	1.6 x 10^{-15}

The painting was stored in a display cabinet at a low pH environment. Over the weekend, the electrical supply of the display cabinet was disrupted which resulted in an increase of the environment's pH. It was found that the green portions of the painting were decolourised due to the formation of solid barium orthoperiodate, $Ba_5(IO_6)_2$.

Explain qualitatively why the green coloured areas of the painting were decolourised but not the red coloured areas when the pH increased.

2 Ag_2CO_3 is a sparingly soluble salt. A 100 cm^3 saturated solution of Ag_2CO_3 in water was found to contain 2.57×10^{-4} mol dm^{-3} of Ag^+ ions.

(i) Calculate the K_{sp} of Ag_2CO_3 and state its units.

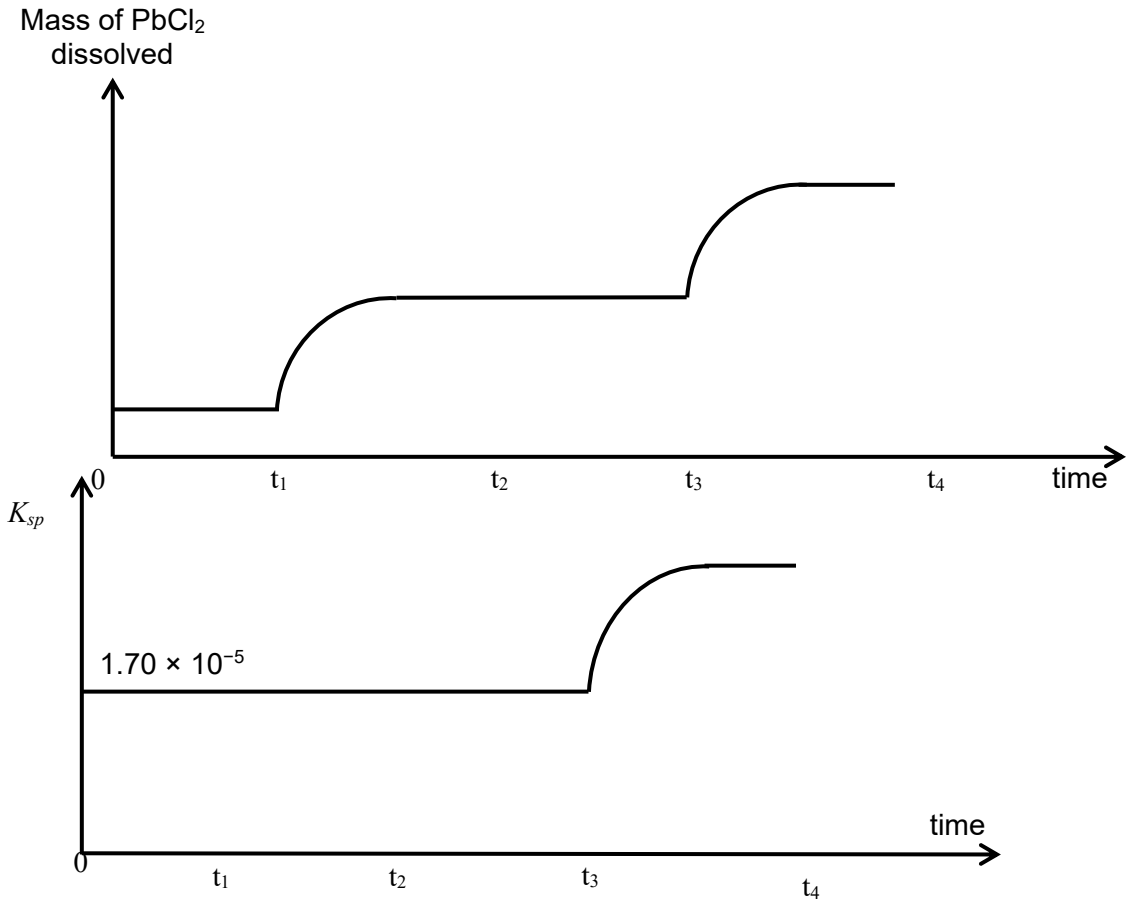
(ii) Hence, calculate the solubility of Ag_2CO_3 when 2.50 g of Na_2CO_3 solid was added to the solution above.

3 $PbCl_2$ is a sparingly soluble salt.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad \Delta H > 0$$

A student investigated the solubility product and solubility of $PbCl_2$ under different conditions. He first added 0.0100 g of solid $PbCl_2$ into 120 cm^3 of an unknown concentration of HCl(aq) at 25 °C and subsequently made four changes at t_1, t_2, t_3 and t_4.

The graphs below show the mass of $PbCl_2$ dissolved and solubility product of $PbCl_2$ against time.



(a) Given that 0.00465 g of $PbCl_2$ remained undissolved after addition of 0.0100 g of $PbCl_2$ into HCl, deduce the unknown concentration of the HCl.

(b) Determine the mass of $PbCl_2$ that can dissolve in 500 cm^3 of water at 25 ^oC.

(c) Some possible changes listed below were made by the student at t_1, t_2 and t_3.

1. Cool reaction mixture to 10 ^oC in water bath
2. Heat reaction mixture to 50 ^oC in water bath
3. Addition of $AgNO_3(aq)$
4. Addition of $PbCl_2(s)$
5. Addition of water

With reference to both graphs, suggest and explain the changes made at t_1, t_2 and t_3.

(d) The student added concentrated HCl at t_4. On both the graphs, draw how the two graphs would look like after t_4.

4 Adding a reagent that selectively brings one of the ions out of a solution as a precipitate while leaving the other ion in the solution is a technique known as selective precipitation.

Data about the solubilities in water and solubility products of silver(I) hydroxide and copper(II) hydroxide at 298 K are given below. Only the numerical values of the solubility products are given.

hydroxide	solubility/ mol dm^{-3}	solubility product
AgOH	1.23×10^{-4}	1.52×10^{-8}
$Cu(OH)_2$	1.77×10^{-7}	2.20×10^{-20}

As a general standard, two ions are selectively separated when a maximum 0.01% of the precipitated compound still remains as the aqueous ions.

Determine if selective precipitation can be performed on solution containing 0.200 mol dm^{-3} Ag^+ and 0.200 mol dm^{-3} Cu^{2+} with the addition of solid potassium hydroxide.

5 Zinc compounds are often used in paints for various purposes. The properties of some of these compounds are given below.

compound	solubility product, K_{sp}	use in paints
$Zn(OH)_2$	3.00×10^{-17}	White pigment
ZnS	3.21×10^{-23}	Luminous pigment
$ZnCO_3$	1.46×10^{-10}	Fire Retardant

(i) Write an expression for K_{sp} for $Zn(OH)_2$ and determine its solubility. Hence, calculate the pH of a saturated solution of $Zn(OH)_2$

(ii) In preparation of a water–based luminous paint mixture, all of the above compounds have to be precipitated. Given that concentration of Zn^{2+} is 2.00×10^{-7} mol dm^{-3}, calculate the minimum amount of S^{2-} that must be present in 250 cm^3 of this mixture.

6 Ammonia is commonly used in qualitative analysis of halides in aqueous solutions, such as detecting the presence of chloride and bromide ions in natural water sources such as rivers, lakes and streams.

(i) 5 cm^3 of 0.0100 mol dm^{-3} of silver nitrate is added to a 30 cm^3 sample of river water containing chloride ions.

What is the minimum concentration, in mol dm^{-3}, of chloride ions present in the river water when the first trace of precipitate appears?

Given solubility product of the silver chloride is 2.0×10^{-10} mol^2 dm^{-6}.

(ii) To a test tube containing another river sample containing bromide ions, describe what you would see when aqueous silver nitrate is added to the sample, followed by excess aqueous ammonia to the resulting mixture

(iii) Explain, with aid of appropriate equation(s), the observations in **(b)(ii)**.

You should use the concepts of Le Chatelier's Principle and solubility product, K_{sp}, to explain your answer.

7 **(i)** Write the expression of the solubility product of calcium oxalate (CaC_2O_4) and express the solubility of calcium oxalate, ***z***, in terms of the solubility product.

(ii) In 1942, Wilbur *et al* reported in the *Journal of American Chemical Society* the effect of pH on the solubility of calcium oxalate. Wilbur proposed that the solubility of calcium oxalate in any solution, in the absence of excess calcium or oxalate ions, should follow the equation below.

$$s = \sqrt{K_{sp}\left(\frac{[H^+] + K_2}{K_2}\right)} \qquad \text{where } K_2 = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

Explain and account for the difference in the expression of solubility for calcium oxalate obtained in **(b)(i)** and that proposed by Wilbur. You must explain why the inclusion of some terms was necessary in Wilbur's equation.

(iii) Hence, state and explain the effect of decreasing pH on the solubility of calcium oxalate.

(iv) Identify a potential problem, in the determination of the solubility of calcium oxalate at high pH, when sodium hydroxide is directly added to a solution of calcium oxalate.

8 Consider the equilibrium dissolution of calcium iodate:

$$Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$$

The standard enthalpy change, $\Delta H^{\ominus}$ and the standard entropy change, $\Delta S^{\ominus}$ for the process were +80 kJ mol^{-1} and + 152 J mol^{-1} K^{-1} respectively. $\Delta G^{\ominus}$, in Joules per mole, and K_{sp} are related by the following equation

$$\Delta G^{\ominus} = -2.303\ RT\ \lg K_{sp}$$

Calculate the value of the solubility product of calcium iodate(V) at 25 °C, stating its units.

9 This question is about the chemistry of Kuro Tamago (lit. “black eggs”), a local specialty of egg hard–boiled in the hot springs of Owankundai, Japan.

When raw eggs are boiled in hot spring water of Owankundai (pH = 9.2), a chemical reaction between aqueous iron(II) and sulfide ions (from hydrogen sulfide, H_2S), produces a black solid, FeS, that adheres to the porous egg shells.

Iron sulfide is precipitated by the following reaction.

reaction 1: $Fe^{2+}(aq) + S^{2-}(aq) \rightarrow FeS(s)$

Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid.

$$H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

In a saturated solution of hydrogen sulfide,

$$[H^+]^2[S^{2-}] = 1.0 \times 10^{-23}\ mol^3\ dm^{-9}$$

(a) Calculate the maximum concentration of sulfide ions present in hot spring water.

(b) Hence, calculate the minimum concentration of Fe^{2+} present in hot spring water in order for precipitation to occur.
(K_{sp} of FeS = $4.9 \times 10^{-18}\ mol^2\ dm^{-6}$)

10 $Al(OH)_3$ is a sparingly soluble aluminium compound with a K_{sp} value of 3×10^{-33} that can be used as a feedstock for manufacturing other aluminium compounds, such as aluminium chloride, zeolites, sodium aluminate.

(a) Write an expression for the K_{sp} of $Al(OH)_3$, stating the units.

(b) Use the data above to determine the solubility of $Al(OH)_3$ in water.

(c) Predict, with a reason, how the solubility of $Al(OH)_3$ will change when it is dissolved in 0.10 mol dm^{-3} of $Al(NO_3)_3$.

11 Most silver salts such as silver chromate(VI), Ag_2CrO_4 are sparingly soluble in water. In an experiment, 8.12 x 10^{-3} mol of potassium chromate(VI), K_2CrO_4, was dissolved in 500 cm^3 of a saturated solution of Ag_2CrO_4.The solubility product of Ag_2CrO_4 is 3.01 × 10^{-12} mol^3 dm^{-9} at 25°C.

(i) Calculate the solubility of Ag_2CrO_4 in water **before** the addition of K_2CrO_4.

(ii) Calculate the solubility of Ag_2CrO_4 **after** the dissolution of K_2CrO_4.

(iii) Use your answers in part **(b)(i)** and **(b)(ii)** to calculate the mass of Ag_2CrO_4 precipitated after the dissolution of K_2CrO_4.

Answers to Solubility Equilibrium

Section A: Multiple Choice Question

1	**D**	**6**	**D**	**11**	**C**	**16**	**B**
2	**C**	**7**	**D**	**12**	**C**		
3	**D**	**8**	**D**	**13**	**D**		
4	**A**	**9**	**B**	**14**	**D**		
5	**C**	**10**	**A**	**15**	**B**		

Worked solution for MCQ:

1 $S = [Mg^{2+}]^3 [AsO_4^{3-}]^2$

Let the solubility of $Mg_3(AsO_4)_2$ be x mol dm^{-3}

$S = (3x)^3 (2x)^2$ ➔ $108\ x^5 = S$

$x = (1/108\ S)^{1/5}$

$[AsO_4^{3-}] = 2x = (32/108\ S)^{1/5} = (8/27\ S)^{1/5}$

Answer is D

2 $[SO_4^{2-}] = 0.5$ mol dm^{-3}, $[CO_3^{2-}] = 1.0$ mol dm^{-3} and $[IO_3^-] = 1.5$ mol dm^{-3}

$[Ba^{2+}]$ to precipitate out $BaSO_4 = 1.1 \times 10^{-10} / 0.5 = 2.2 \times 10^{-10}$ mol dm^{-3}

$[Ba^{2+}]$ to precipitate out $BaCO_3 = 2.6 \times 10^{-9} / 1.0 = 2.6 \times 10^{-9}$ mol dm^{-3}

Let the solubility of $Ba(IO_3)_2$ be x mol dm^{-3}

$K_{sp} = [Ba^{2+}] [IO_3^-]^2 = (x) (2x + 1.5)^2$

$= (x) (1.5)^2$ (ssuming $2x << 1.5$)

$x = 4.0 \times 10^{-9} / 2.25 = 1.77 \times 10^{-9}$

$[Ba^{2+}]$ to precipitate out $Ba(IO_3)_2 = 1.77 \times 10^{-9}$ mol dm^{-3}

Answer is C

3 When pH decreases, $[H^+]$ increases and $[OH^-]$ decreases, equilibrium position of second equation shift to the right and [HC*l*O] increases. Bacterial growth will be **less favourable**.

When [C*l*O$^-$] decreases, equilibrium position of first equation shift to the right and **solubility of calcium hypochlorite increases**.

Answer is D

4

	$Mg_3(PO_4)_2 \rightleftharpoons$	$3\ Mg^{2+}$	$+\ 2\ PO_4^{3-}$
Change	$-\ x$	$+\ 3x$	$+\ 2x$
Equilibrium		$3x$	$2x$

$K_{sp} = [Mg^{2+}]^3\ [PO_4^{3-}]^2$

$Q = (3x)^3\ (2x)^2$

$Q = (27x^3)\ (4x)$

$x = (\frac{Q}{108})^{\frac{1}{5}}$

$[Mg^{2+}] = 3 \times (\frac{Q}{108})^{\frac{1}{5}}$

$= (\frac{243Q}{108})^{\frac{1}{5}}$

$= (\frac{9Q}{4})^{\frac{1}{5}}$

Answer is A

5 $[Sr^{2+}]$ remaining in solution = $1.6 \times 10^{-9} / 2.5 \times 10^{-6} = 0.00064$ mol dm^{-3}

Amount of $Sr^{2+} = 0.00064 \times 0.5 = 0.00032$ mol

Amount of Sr^{2+} precipitated out = Amount of $SrCO_3$ precipitated out

$= (2.0 \times 10^{-2} \times 0.5) - 0.00032 = 0.00968$ mol

Mass of $SrCO_3$ precipitated out = $(0.00968)(12.0 + 16.0 \times 3 + 87.6) = 1.43$ g

Answer is C

6 Option **1**: Correct

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

Let the solubility of $Ca(OH)_2$ be y mol dm^{-3}.

$[Ca^{2+}][OH^-]^2 = 4.7 \times 10^{-6}$

$(y)(2y)^2 = 4.7 \times 10^{-6}$

y = 0.0106 mol dm^{-3}
$[OH^-]$ = 2y = 0.021 mol dm^{-3}

Option **2**: Incorrect

When equal volumes of solutions are mixed together, dilution occurs and their concentrations are halved. Hence, new $[Ca^{2+}]$ = 0.01 mol dm^{-3} and new $[OH^-]$ = 0.01 mol dm^{-3}.

Ionic product = $[Ca^{2+}][OH^-]^2 = (0.01)(0.01)^2$
$= 1.0 \times 10^{-6} < 4.7 \times 10^{-6}$ mol^3 dm^{-9}

Since ionic product < $K_{sp}(Ca(OH)_2)$, precipitation will not occur.

Option **3**: Incorrect

$Sn(OH)_2$ has the lowest solubility amongst the three metal hydroxides.

metal hydroxide	K_{sp}	Solubility / mol dm^{-3}
$Ca(OH)_2$	4.7×10^{-6} mol^3 dm^{-9}	0.0106
$Sn(OH)_2$	5.4×10^{-27} mol^3 dm^{-9}	1.11×10^{-9}
$Cr(OH)_3$	6.7×10^{-31} mol^4 dm^{-12}	1.26×10^{-8}

7 NH_4^+ is the conjugate acid of a weak base, NH_3.
NH_4^+ dissociates partially in water to produce H_3O^+ as follows:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$Mg(OH)_2(s)$ then undergoes an acid–base reaction (neutralisation) with the H_3O^+ ions produced.

$$Mg(OH)_2(s) + 2H_3O^+(aq) \longrightarrow Mg^{2+}(aq) + 4H_2O(l)$$

Answer is D

8 A saturated solution of $Ca(OH)_2$ is found to have a pH of 12.3 at 25 °C.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^- \text{..... eqm (1)}$$

Option A is correct: K_{sp} of $Ca(OH)_2 = [Ca^{2+}][OH^-]^2$
$= (1/2 \times 10^{-1.7}) (10^{-1.7})^2 = 4 \times 10^{-6}$ mol^3 dm^{-9}.

Option B is correct: The solubility of $Ca(OH)_2$ would increase when temperature is raised to 35 °C.

Option C is correct: When solid Na_2O is added, NaOH is formed, hence $[OH^-]$ increases. As such, POE of eqm (1) above will shift to the left, hence $[OH^-]$ decrease. The solubility of $Ca(OH)_2$ will decrease.

Option D is incorrect: When $Ca(NO_3)_2$ is added, $[Ca^{2+}]$ increases. As such, POE of eqm (1) above will shift to the left, hence $[OH^-]$ decrease. The pH of the solution would decrease.

9 Let x be $[Pb^{2+}]$

$K_{sp} = [Pb^{2+}] [CrO_4^{2-}] = (x) (0.010) = 1.69 \times 10^{-14}$

$x = 1.69 \times 10^{-12}$

Answer is B

10 Option 1 is correct, because as $[H^+]$ increases, by LCP, POE shifts to the right to partially decrease $[H^+]$, and concentration of hydroxyapatite decreases, leading to speeding up of tooth decay.

Option 2 is correct: same reasoning as option 1.

Option 3 is correct, as H^+ is unable to react with OH^- in hydroxyapatite to form water and indirectly cause tooth decay.

11 $K_{sp} = [Pb^{2+}] [OH^-]^2 = (1.06 \times 10^{-5}) (2 \times 1.06 \text{ x } 10^{-5})^2 = 4.764 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$

$$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$$

$[OH^-] = 1 \times 10^{-14} / 10^{-12.8} = 0.06310 \text{ mol dm}^{-3}$

Solubility of $Pb(OH)_2 = 4.764 \times 10^{-15} / (0.06310)^2 = 1.19 \times 10^{-12} \text{ mol dm}^{-3}$

Answer is C

12 $[Cl^-] = \sqrt{(1.6 \text{ x } 10^{-10})} = 1.265 \times 10^{-5} \text{ mol dm}^{-3}$

$[I^-] = \sqrt{(8.0 \text{ x } 10^{-17})} = 8.94 \times 10^{-9} \text{ mol dm}^{-3}$

$K_c = [Cl^-] / [I^-] \sim 1400$

Answer is C

13 $K_{sp} = [Pb^{2+}] [Br^-]^2 = [Pb^{2+}] (1 \times 10^{-3})^2$

$[Pb^{2+}] = 4.0 \times 10^{-5} / 1 \times 10^{-6} = 40 \text{ mol dm}^{-3}$

$[Pb^{2+}]$ to precipitate out $PbF_2 = 2.7 \times 10^{-8} / 1 \times 10^{-6} = 0.027 \text{ mol dm}^{-3}$

$[Pb^{2+}]$ to precipitate out $PbI_2 = 7.1 \times 10^{-9} / 1 \times 10^{-6} = 0.0071 \text{ mol dm}^{-3}$

$[Pb^{2+}]$ to precipitate out $PbSO_4 = 1.6 \times 10^{-8} / 1 \times 10^{-3} = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$

Answer is D

14

$$Ag_2C_2O_4 \rightleftharpoons 2Ag^+ + C_2O_4^{2-}$$

$K_{sp} = [Ag^+]^2 [C_2O_4^{2-}]$

Let the solubility of $Ag_2C_2O_4$ be x mol dm^{-3}.

$6.10 \times 10^{-12} = (2x)^2 (x) = 4x^3$

$x = \sqrt[3]{(6.10 \times 10^{-12} / 4)} = 1.151 \times 10^{-4}$ mol dm^{-3}

$[Ag^+] = 1.151 \times 10^{-4} \times 2 = 2.30 \times 10^{-4}$ mol dm^{-3}

Answer is D

15 $[SO_4^{2-}] = 0.100$ mol dm^{-3},

$[Ag^+] = 1.00 \times 10^{-2}$ mol dm^{-3} and $[Ca^{2+}] = 9.00 \times 10^{-3}$ mol dm^{-3}

Ionic product of $Ag_2SO_4 = [Ag^+]^2 [SO_4^{2-}] = (1.00 \times 10^{-2})^2 (0.100) = 1 \times 10^{-5}$ mol^3 dm^{-9}

Since ionic product of Ag_2SO_4 is less than K_{sp}, Ag_2SO_4 will not be precipitated.

Ionic product of $CaSO_4 = [Ca^{2+}] [SO_4^{2-}] = (9.00 \times 10^{-3}) (0.100) = 9 \times 10^{-4}$ mol^3 dm^{-9}

Since ionic product of Ag_2SO_4 is greater than K_{sp}, $CaSO_4$ will be precipitated.

Answer is B

16 $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

Let the solubility of $CaCO_3$ be x mol dm^{-3} and solubility of CaF_2 be y mol dm^{-3}.

$8.7 \times 10^{-9} = (x) (x) = x^2$

$x = \sqrt{(8.7 \times 10^{-9})} = 9.33 \times 10^{-5}$ mol dm^{-3}

$4.0 \times 10^{-11} = (y) (2y)^2 = 4y^3$

$y = \sqrt[3]{(4.0 \times 10^{-11} / 4)} = 2.15 \times 10^{-4}$ mol dm^{-3}

Option A is wrong since CaF_2 has higher solubility.

Option B is correct, since $K_{sp} = [Ca^{2+}] [F^-]^2$ and adding more F^- will cause ionic product to increase.

Option C is wrong, since solubility product does not change with the same temperature.

$[Ca^{2+}]$ to precipitate out $CaCO_3 = 8.7 \times 10^{-9} / 1 = 8.7 \times 10^{-9}$ mol dm^{-3}

$[Ca^{2+}]$ to precipitate out $CaF_2 = 4.0 \times 10^{-11} / 1^2 = 4.0 \times 10^{-11}$ mol dm^{-3}

CaF_2 will precipitate out first, so option D is wrong.

Answer is B

Worked solution for Structured Questions:

1 When pH increases, $[H^+]$ decreases, resulting in the eqm shifting right to produce H^+ ions. Thus concentration of IO_6^{5-} ions is high as the position of eqm shifts towards the right.
Thus IP of $Ba_5(IO_6)_2$ is higher than K_{sp}, precipitate of barium orthoperiodate, $Ba_5(IO_6)_2$ forms and the green coloured area containing barium ions were decolourised.

However, $Ca_5(IO_6)_2$ has higher K_{sp} value and do not precipitate easily even with increase in concentrations of IO_6^{5-} ions. The resulting ionic product of Ca^{2+} ions and IO_6^{5-} ions still does not exceed the K_{sp}. Precipitate of $Ca_5(IO_6)_2$ is not formed and the red coloured area containing calcium ions is not being affected.

2 **(i)** $K_{sp} = [Ag^+]^2[CO_3^{2-}] = (2.57\times10^{-4})^2(2.57\times10^{-4}/2) = 8.49 \times 10^{-1[2]}ol^3\ dm^{-9}$

(ii) $K_{sp} = [Ag^+]^2[CO_3^{2-}]$
$8.49 \times 10^{-12} = [Ag^+]^2 \times (2.50 \div (23 \times 2 + 12 + 16 \times 3) \div (100/1000))$
$[Ag^+] = 6.00 \times 10^{-6}$ mol dm^{-3}
Solubility of $Ag_2CO_3 = ½ \times 6.00 \times 10^{-6} = 3.00 \times 10^{-6}$ mol dm^{-3}

3 **(a)** Mass of $PbCl_2$ dissolved = 0.0100 – 0.00465 = 0.00535 g

Solubility of $PbCl_2$ in HCl(aq), $x = \frac{0.00535/278.0}{120/1000} = 1.604 \times 10^{-4}$ mol dm^{-3}

Let x be the unknown concentration of HCl(aq),

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$
1.604×10^{-4} mol dm^{-3} $2(1.604 \times 10^{-4})$ mol dm^{-3}

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
x mol dm^{-3} x mol dm^{-3} x mol dm^{-3}

At saturation, ionic product = K_{sp}

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.70 \times 10^{-5} = (1.604 \times 10^{-4})(2 \times 1.604 \times 10^{-4} + x)^2$

Assuming $2(1.604 \times 10^{-4})$ is small,

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.70 \times 10^{-5} = (1.604 \times 10^{-4})(x)^2$

$x = 0.3256 =$ **0.326 mol dm^{-3}**

(b) Let m be the mass of $PbCl_2$ dissolve in 500 cm^3 of water.

$PbCl_2\ (s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

Solubility of $PbCl_2$ in water $= \frac{m/278.0}{500/1000}$

K_{sp} remain unchanged at 25 °C.

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$4\ (\frac{m/278.0}{500/1000})^3 = 1.70 \times 10^{-5}\ mol^2\ dm^{-6}$

m = 2.252 g = <u>2.25 g</u>

(c) Change made at t_1: Addition of water or Addition of $AgNO_3(aq)$

The total volume increase when water is added to reaction mixture, hence $[Pb^{2+}]$ and $[Cl^-]$ decrease. According to Le Chatelier's Principle, position of equilibrium shifts right to increase the $[Pb^{2+}]$ and $[Cl^-]$. Thus, more $PbCl_2$ dissolve. K_{sp} remain constant as K_{sp} is temperature dependent.

OR

Presence of Ag^+ caused precipitation of AgCl(s), hence $[Cl^-]$ decrease. According to Le Chatelier's Principle, position of equilibrium shifts right to increase $[Cl^-]$. Thus, more $PbCl_2$ dissolve and K_{sp} remain constant as K_{sp} is temperature dependent.

Change made at t_2: Addition of $PbCl_2(s)$

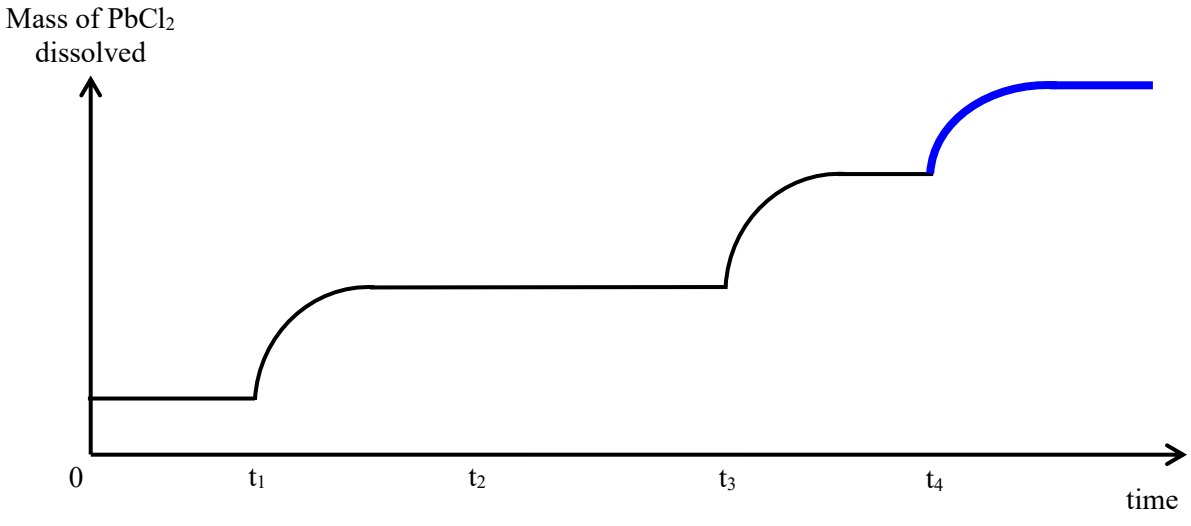
The solution is already saturated. Hence, as more $PbCl_2(s)$ is added, the mass of $PbCl_2$ dissolve will not increase. K_{sp} remain constant as K_{sp} is temperature dependent.

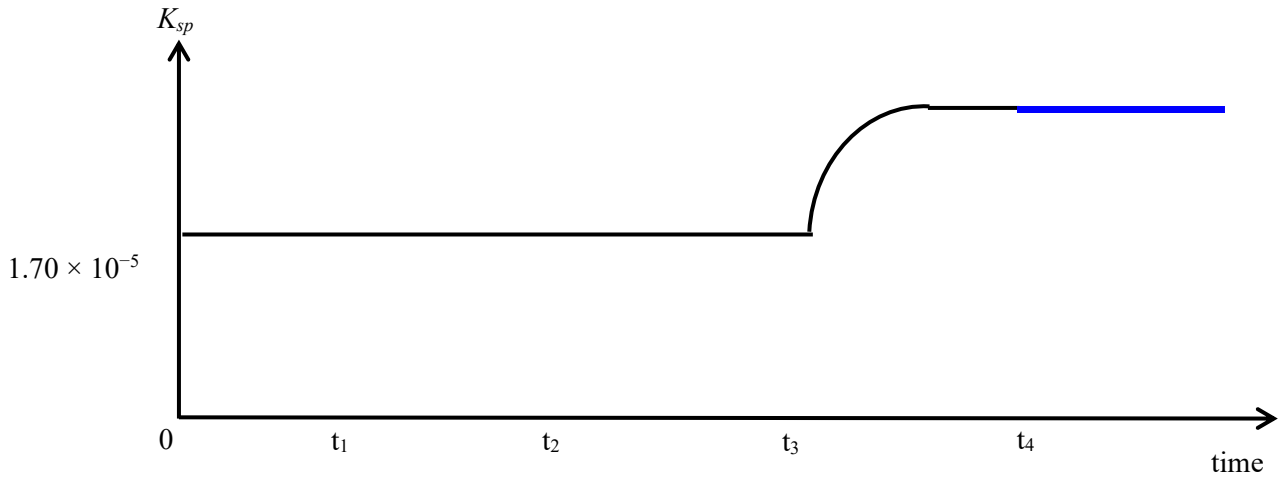
Change made at t_3: Heat reaction mixture to 50 °C in water bath

According to Le Chatelier's Principle, as temperature increases, the position of equilibrium shifts right to favour the forward endothermic reaction, to absorb heat. Hence, $[Pb^{2+}]$ and $[Cl^-]$ increase. The mass of $CaSO_4$ dissolved and K_{sp} increase.

(d) $PbCl_2 + 2Cl^- \rightleftharpoons PbCl_4^{2-}$

Formation of complex, $PbCl_4^{2-}$, increases the solubility of $PbCl_2$. Hence, mass of $PbCl_2$ dissolve increase. K_{sp} remain constant as K_{sp} is temperature dependent.





4 Since solubility of $Cu(OH)_2$ is lower than AgOH, it will be precipitated first.

To maximally precipitate $Cu(OH)_2$, AgOH has to be saturated.

$[OH^-]$ when AgOH is saturated = $\frac{1.52 \times 10^{-8}}{0.200}$ = 7.60×10^{-8} mol dm^{-3}

$[Cu^{2+}]$ when AgOH is saturated = $\frac{2.20 \times 10^{-20}}{\left(7.60 \times 10^{-8}\right)^2}$ = 3.81×10^{-6} mol dm^{-3}

%$[Cu^{2+}]$ remaining = $\frac{3.81 \times 10^{-6}}{0.200} \times 100\%$ = 0.001905% ≈ 0.00191% < 0.01%

Therefore Cu^{2+} can be selectively precipitated from Ag^+.

5 **(i)** $Zn(OH)_2$ (s) ⇌ Zn^{2+} (aq) + $2OH^-$(aq)
$K_{sp} = [Zn^{2+}][OH^-]^2$

Let solubility of $Zn(OH)_2$ be x mol dm^{-3}
$K_{sp} = (x)(2x)^2$
$3.00 \times 10^{-17} = 4x^3$
$x = \sqrt[3]{\frac{3.00 \times 10^{-17}}{4}} = 1.96 \times 10^{-6}$ mol dm^{-3}
$[OH^-] = 2x = 2(1.96 \times 10^{-6}) = 3.92 \times 10^{-6}$ mol dm^{-3}

pOH = – lg (3.92×10^{-6}) = 5.41
pH = 14 – 5.41 = 8.59

(ii) For precipitation, $[Zn^{2+}][S^{2-}] > K_{sp}$
$[S^{2-}] > 3.21 \times 10^{-23} / 2.00 \times 10^{-7}$
$[S^{2-}] > 1.605 \times 10^{-16}$

Minimum amount of $S^{2-} = 1.605 \times 10^{-16} \times 250 / 1000 = 4.0125 \times 10^{-17}$
$= 4.02 \times 10^{-17}$ mol

6 **(i)** $Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$
ppt is AgX.

[Ag^+] at point of mixing = no. of moles of Ag^+ before mixing ÷ total vol
= (0.0100 x 5/1000) ÷ 35/1000
= 1.428×10^{-3} mol dm^{-3}

[Cl^-] at point of mixing = no. of moles of X^- before mixing ÷ total vol.
= ([Cl^-]$_{initial}$ x 30/1000) ÷ 35/1000 mol dm^{-3}

For precipitation to take place, Ionic product (AgCl) ≥ Ksp(AgCl)

([Ag^+][Cl^-]) at point of mixing ≥ 2.0×10^{-10}

$$(1.428\times10^{-3})\times\left(\frac{[Cl^-]_{initial}\times\frac{30}{1000}}{\frac{35}{1000}}\right) \geq 2.0 \times 10^{-10}$$

[Cl^-]$_{initial}$ ≥ 1.63×10^{-7}

Hence, minimum concentration is 1.63×10^{-7} mol dm^{-3}

(ii) Br^-: <u>cream ppt</u> of AgBr observed; <u>insoluble</u> in excess $NH_3(aq)$

(iii) $Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s)$ ....(1)

Precipitate of AgBr is observed when I.P> K_{sp}

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ ….(2)
When excess NH_3 is added (high [NH_3]) to AgBr(s), position of eqm (2) shifts to the **<u>right</u>** in order to reduce the effect of excess $NH_3(aq)$. OR complex $[Ag(NH_3)_2]^+$ is formed

[Ag^+] decreases hence equilibrium (1) shifts to the left.
but the ionic product of AgBr is still **<u>larger than</u>** K_{sp}(AgBr),
AgBr remains insoluble.

OR

$AgBr(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

7 **(i)** $K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$

$z = \sqrt{K_{sp}}$

(iii) The oxalate anion is a conjugate base of the weak acid hydrogen oxalate. Since the extent of dissociation of hydrogen oxalate depends on the pH of the solution, the concentration of oxalate ion resulting from the dissociation of hydrogen oxalate will also depend on the pH of the solution.

Therefore, the term K_2 must be taken into account when considering the solubility of oxalate. The term $[H^+]$ is to account for the pH of the solution that calcium oxalate is subjected to.

(iv) Solubility of calcium oxalate will increase with decreasing pH value (can be inferred from the given equation due to the increase in $[H^+]$.)

$CaC_2O_4\,(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}\,(aq)$

- At low pH, oxalate ions will be protonated to form hydrogen oxalate ions.
- This will reduce the concentration of oxalate ions.
- By Le Chatelier's principle, equilibrium shift to increase the concentration of oxalate ions.
- Hence, the solubility of calcium oxalate will increase.

(iv) NaOH might precipitate $Ca(OH)_2(s)$ which would decrease the concentration of calcium ions, thereby potentially increasing the solubility of calcium oxalate at high pH.

8 $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta = +80000 - (273+25)(152) = 34\ 704$ J mol^{-1}

$\Delta G^\theta = -2.303\ RT\ \lg K_{sp}$
$34\ 704 = -2.303\ (8.31)(298)\ \lg K_{sp}$
$K_{sp} = 8.22 \times 10^{-7}$ mol^3 dm^{-9}

9 **(a)** $[H^+] = 10^{-9.2}$
$= 6.31 \times 10^{-10}$ mol dm^{-3}

$[S^{2-}] = \dfrac{1.0 \times 10^{-23}}{(6.31 \times 10^{-10})^2} = 2.51 \times 10^{-5}$ mol dm^{-3}

(b) $K_{sp} = [Fe^{2+}][S^{2-}]$

$[Fe^{2+}] = \dfrac{4.9 \times 10^{-18}}{2.51 \times 10^{-5}} = 1.95 \times 10^{-13}$ mol dm^{-3}

10 **(a)** $K_{sp} = [Al^{3+}]\,[OH^-]^3$
Unit: mol^4 dm^{-12}

(b) $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$
x $\quad 3x$

Let the solubility of $Al(OH)_3$ be x mol dm^{-3}

$K_{sp} = [Al^{3+}][OH^-]^3$

$3 \times 10^{-33} = (x) \times (3x)^3$

$27x^4 = 3 \times 10^{-33}$

$x = 3.25 \times 10^{-9}$ mol dm^{-3}

Solubility = 3.25×10^{-9} mol dm^{-3}

(c) $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$

Solubility of $Al(OH)_3$ will **<u>decrease</u>** (due to common ion effect)

<u>High $[Al^{3+}]$ from $Al(NO_3)_3$</u> will shift the **<u>position of the above eqm to the left</u>.**

11 (i) $K_{sp} = 3.01 \times 10^{-12} = 4s^3$
$s = 9.10 \times 10^{-5}$ mol dm^{-3}

(iii) $[K_2CrO_4] = 8.12 \times 10^{-3} / 0.500 = 0.01624$ mol dm^{-3}

Let s' be the new solubility of Ag_2CrO_4
$3.01 \times 10^{-12} = (2s')^2(s' + 0.01624)$.

Assume $(s' + 0.01624) \approx 0.01624$

$3.01 \times 10^{-12} = (2s')^2(0.01624)$
$s' = 6.81 \times 10^{-6}$ mol dm^{-3}

(iii) Difference in Ag_2CrO_4 solubility $= 9.10 \times 10^{-5} - 6.81 \times 10^{-6}$
$= 8.42 \times 10^{-5}$ mol dm^{-3}

No. of moles of Ag_2CrO_4 precipitated $= 8.42 \times 10^{-5} \times 0.500$
$= 4.21 \times 10^{-5}$ mol

Mass of Ag_2CrO_4 precipitated $= 8.138 \times 10^{-5} \times 332$
$= 0.0140$ g

4. ELECTROCHEMISTRY:

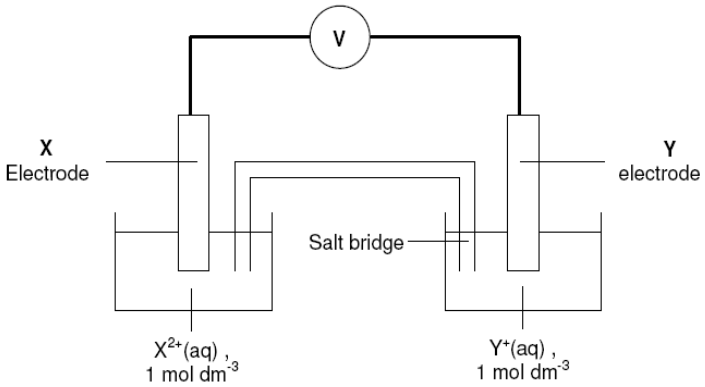
(A) Electrochemical Cells

Section A: Multiple Choice Questions

1 The standard electrode potential for the metals **X** and **Y** are given below.

$\mathbf{X}^{2+}(aq) / \mathbf{X}(s)$; $E^{\ominus} = -0.25$ V; $\mathbf{Y}^{+}(aq) / \mathbf{Y}(s)$; $E^{\ominus} = +0.80$ V

The diagram of the cell made up of the above two half–cells is shown below.



Which description is correct for this cell?

	Cathode	E^{θ}_{cell}	Direction of electron flow	Electrode at which cations enter solution
A	**X**	+0.55 V	**X** to **Y**	**X**
B	**X**	+1.05 V	**Y** to **X**	**Y**
C	**Y**	+1.05 V	**X** to **Y**	**X**
D	**Y**	+0.55 V	**Y** to **X**	**Y**

2 Some standard reduction potentials are given in the table below.

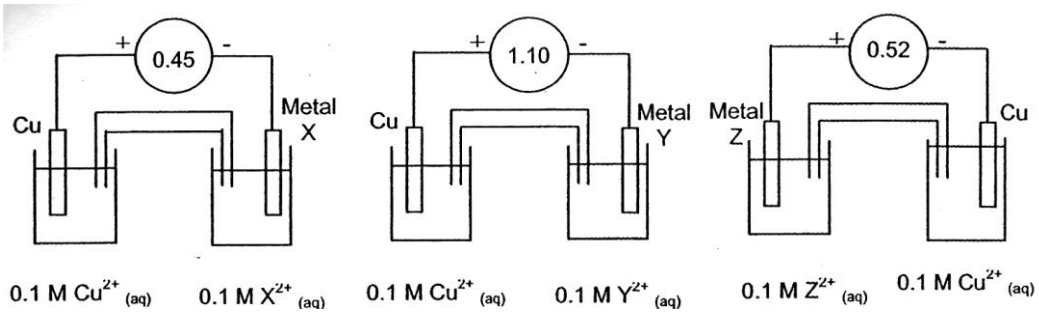
Half–equation			$E^{\ominus}$ / V
$2H_2SO_3 + 2H^+ + 4e^-$	⇌	$S_2O_3^{2-} + 3H_2O$	E_1
$[SnCl_6]^{2-} + 2e^-$	⇌	$Sn^{2+} + 6Cl^-$	E_2
$½Hg_2^{2+} + e^-$	⇌	$Hg(l)$	E_3
$Sb_2O_5 + 6H^+ + 4e^-$	⇌	$2[Sb(OH)_2]^+ + H_2O$	E_4

A redox reaction occurs when Sb_2O_5 is mixed with $S_2O_3^{2-}$, but no reaction occurs when Sb_2O_5 is mixed with Hg. A solution of $[SnCl_6]^{2-}$ has no effect on $S_2O_3^{2-}$. Which of the following gives the order of the standard reduction potentials from highest to lowest?

A $E_2 > E_1 > E_4 > E_3$ **B** $E_2 > E_4 > E_1 > E_3$

C $E_3 > E_1 > E_4 > E_2$ **D** $E_3 > E_4 > E_1 > E_2$

3 Three electrochemical cells are set up as shown below. The e.m.f. in volts is shown on each voltmeter.



These e.m.f. indicate that the order of activity of the metals, from weakest reducing agent to strongest reducing agent is

A X, Cu, Y, Z **B** Cu, Z, X, Y **C** Z, Cu, X, Y **D** Y, X, Z, Cu

4 A voltaic cell is made up of the Mg^{2+}/Mg half–cell and the Fe^{3+}/Fe^{2+} half–cell.
Which statement about the voltaic cell is correct?

A Addition of water to the Fe^{3+}/Fe^{2+} half–cell decreases the e.m.f. of the cell.
B Addition of NaOH(aq) to the Mg^{2+}/Mg half–cell increases the e.m.f. of the cell.
C Increasing the temperature has no effect on the e.m.f. of the cell.
D The Mg^{2+}/ Mg half–cell is the positive electrode.

5 The following reaction has a negative E^{θ}_{cell} so that it does not occur under standard conditions.

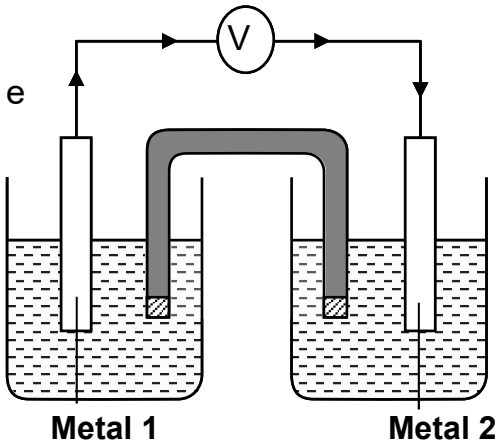
$$2NO_3^-(aq) + 8H^+(aq) + 6Cl^-(aq) \rightleftharpoons 2NO(g) + 4H_2O(l) + 3Cl_2(g)$$

Nevertheless, the reaction may be made to proceed under non–standard conditions.
Which would **not** help the reaction to proceed?

A Increase $[H^+(aq)]$
B Addition of solid potassium nitrate
C Addition of potassium iodide
D Addition of bromine

6 *Use of the Data Booklet is relevant to this question.*

The half–cells for four metals: Mg, **A**, **B** and **C** were in turn connected in pairs and the potential difference under standard conditions was measured and recorded.



The results obtained are as shown in the table below.

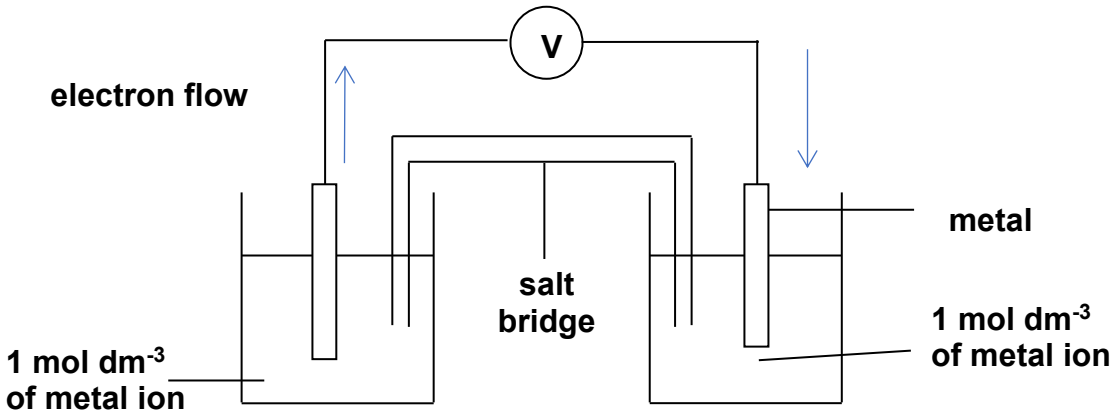
Positive electrode	Negative electrode	e.m.f /V
A	Mg	+2.10
B	Mg	+2.72
Mg	**C**	+0.33

Rank the four metals in the order of decreasing reducing power.

A **B** > **A** > Mg > **C** **B** **A** > **B** > Mg > **C**

C **C** > Mg > **A** > **B** **D** **C** > Mg > **B** > **A**

7 A Fe^{3+}/Fe^{2+} half–cell was connected to a Ni^{2+}/Ni half–cell as shown in the diagram below under standard conditions.



Which statement is **incorrect**?

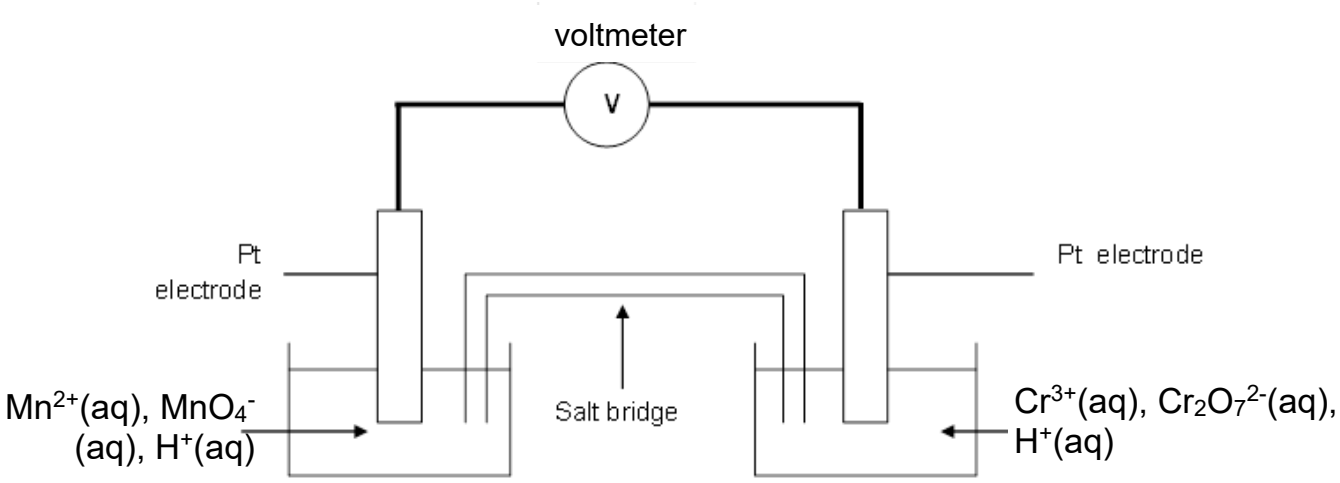
A The solution in the Fe^{3+}/Fe^{2+} half–cell turns green.

B The standard cell potential is +1.02 V.

C The electron flows from the Ni^{2+}/Ni half–cell to the Fe^{3+}/Fe^{2+} half–cell through external circuit.

D The cathode decreases in size after some time.

8 A student set up the cell as shown



The following values for the cell potential were determined as a change was continuously made.

reading number	cell potential /V
1	0.1900
2	0.1890
3	0.1878
4	0.1865
5	0.1850

Which continuous change in the MnO_4^- half–cell could produce these results?

A adding a reagent to the solution that complexes with $Mn^{2+}(aq)$

B increasing the concentration of $Mn^{2+}(aq)$

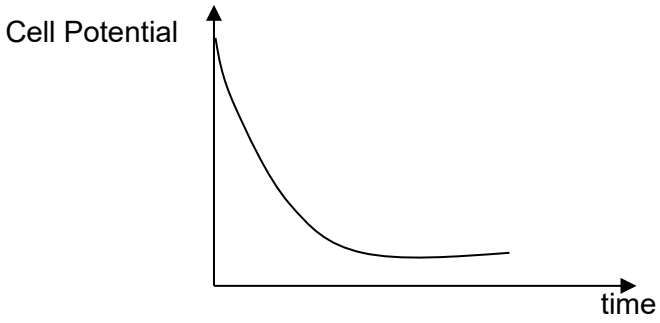
C changing the electrode to Mn metal

D adding more acid to the solution

9 An experiment is carried out with the following cell.

$$Fe(s) \mid Fe^{2+}(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$$

The following graph of cell potential against time was obtained when a change was continuously made to the half–cell.



What continuous change could produce these results?

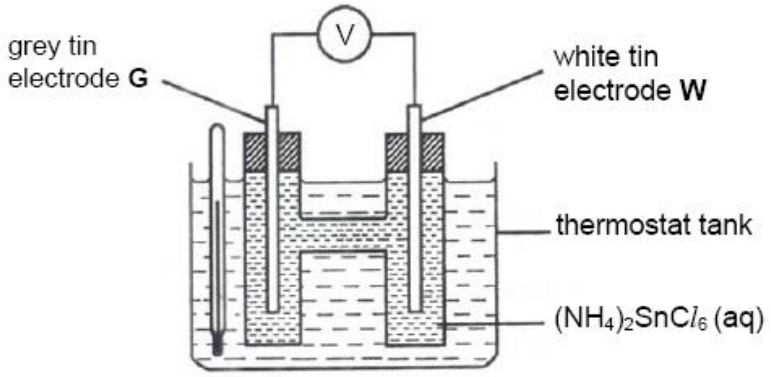
A add solid nickel(II) chloride to the nickel half–cell

B add aqueous cyanide ions to the iron half–cell

C add water to the nickel half–cell

D Increases the surface area of iron immersed in the solution.

10 The diagram shows an apparatus used to find the transition temperature (15 ºC) at which white tin and grey tin are at equilibrium. Below 15 ºC, white tin from **W** dissolves and is deposited on **G** as grey tin.



Which statement is true?

A Increasing the size of the grey tin electrode will change the cell potential.

B At 15 ºC, no current flows.

C Above 15 ºC, electrons flow through the external circuit from **W** to **G**.

D The stable form of tin at 25 ºC is grey.

11 Pain is often felt when a piece of aluminium foil touches a tin–containing dental amalgam filling in a tooth because an electric current momentarily flows. Similarly, when the dentist uses a stainless steel dental tool to work on the filling, pain is felt.

The standard electrode potentials are as follows:

$Al^{3+}(aq) \mid Al(s) = -1.66$ V; $Fe^{2+}(aq) \mid Fe(s) = -0.44$ V; $Sn^{2+}(aq) \mid$ amalgam $= -0.13$ V

Which are features of the cell obtained?

1 The amalgam acts as the positive electrode.

2 The electric current flows momentarily because a small amount of Sn^{2+} ions are present.

3 The standard cell potential involving aluminium foil is smaller than that involving stainless steel

A **1, 2** and **3** are correct

B **1** and **2** are correct

C **2** and 3 are correct

D **1** only is correct

12 Consider the following standard electrode potentials:

P^+/P, +1.80 V ; Q^{2+}/Q, +0.3 V ; R^+/R, –0.90 V ; S^{2+}/S, –0.30 V

Which statements are correct?

1 P and Q could be used as the electrodes for a simple cell of e.m.f. +1.50 V.

2 S could be oxidised by R^+.

3 P^+ is the strongest reducing agent among all the species listed.

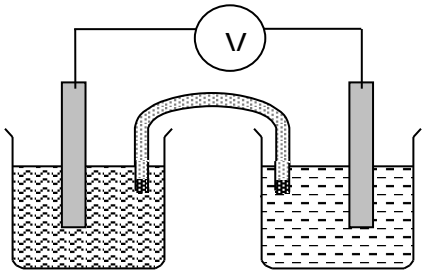
A **1, 2** and **3** are correct

B **1** and **2** are correct

C **2** and 3 are correct

D **1** only is correct

13 A cell involving aqueous potassium iodide and acidified potassium manganate(VII) is shown.



$E^{\ominus}$ (I_2 / I^-) = +0.54 V $E^{\ominus}$(MnO_4^- / Mn^{2+}) = +1.52 V

Which observations about this arrangement are correct?

1 The voltmeter shows a reading of about 0.98 V.

2 The potassium iodide solution turns brown.

3 The purple colour of the potassium manganate(VII) solution becomes less intense

A **1, 2** and **3** are correct

B **1** and **2** are correct

C **2** and 3 are correct

D **1** only is correct

14 Which statements can be deduced from the following standard potentials listed below?

	$E^{\ominus}$ / V
$Cd^{2+}(aq) + 2e \rightleftharpoons Cd(s)$	−0.40
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	−0.28
$Co^{3+}(aq) + e \rightleftharpoons Co^{2+}(aq)$	+1.82
$Ga^{3+}(aq) + 3e \rightleftharpoons Ga(s)$	−0.56
$In^{3+}(aq) + 3e \rightleftharpoons In(s)$	−0.34

1 Co^{2+} is a stronger oxidising agent than Ga^{3+}.

2 In is a weaker reducing agent than Cd.

3 Co^{3+} can be reduced to Co by In.

A **1, 2** and **3** are correct

B **1** and **2** are correct

C **2** and 3 are correct

D **1** only is correct

15 *Use of the Data Booklet is relevant to this question.*

In research laboratories, the standard calomel reference electrode and the AgCl//Ag reference electrodes are often used in place of the standard hydrogen electrode (SHE). Their standard reduction potentials with respect to the SHE are shown below.

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$ $E^\ominus = +0.27$ V
AgCl//Ag electrode: $AgCl + e^- \rightleftharpoons Ag + Cl^-$ $E^\ominus = +0.22$ V

A half–cell containing Au^+/Au has a reduction potential of +1.56 V with respect to a calomel electrode.

Which of the following statements is correct?

A The reduction potential of the Au^+/Au half–cell with respect to the SHE is +1.83 V.

B The reduction potential of the Au^+/Au half–cell with respect to the AgCl//Ag electrode is +1.78 V.

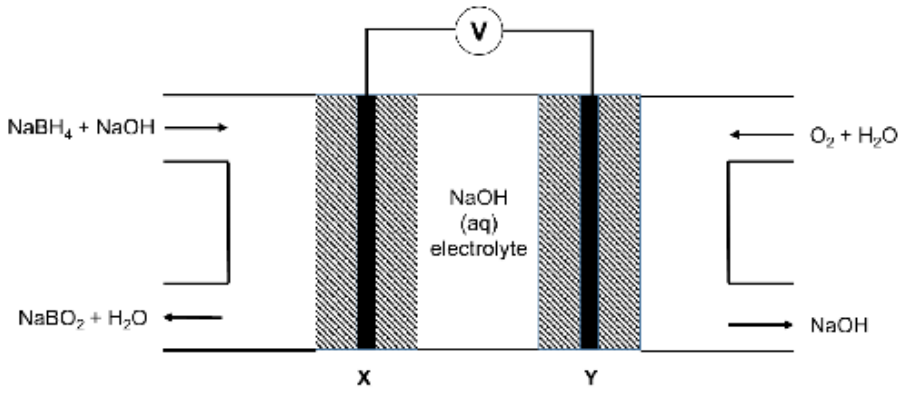
C Ag has a higher tendency to be oxidised than H_2.

D Hg_2Cl_2 has a lower tendency to be reduced than AgCl.

16

Use of the Data Booklet is relevant to this question.

The Direct Borohydride Fuel Cell (DBFC) is a type of alkaline fuel cell that uses $NaBH_4$ as the fuel and O_2 as the oxidant. A DBFC was set up under standard conditions according to the diagram below.



The electrode potential of the $NaBH_4/NaBO_2$ half–cell is given below.

$NaBO_2 + 6H_2O + 8e^- \rightleftharpoons NaBH_4 + 8OH^-$ $E^\ominus = -1.24$ V

Which of the following statements regarding the DBFC are correct?

1 The voltmeter will register a reading of +1.64 V.

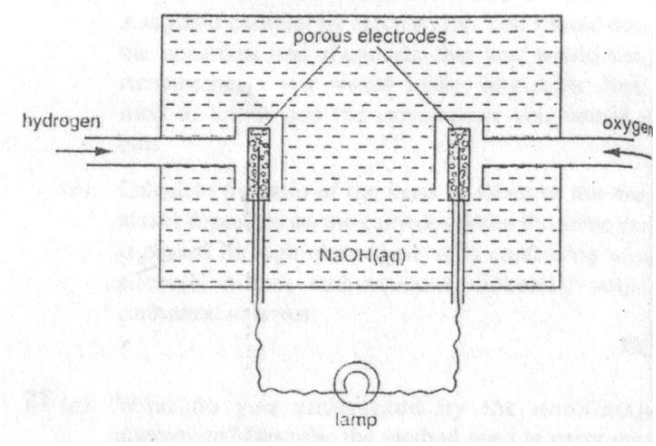
2 Electrode **X** is the anode and electrode **Y** is the cathode in the DBFC.

3 The BO_2^- ion produced at electrode **X** has a bond angle of 180°.

A 1, 2 and 3 are correct **B** 1 and 2 are correct **C** 2 and 3 are correct **D** 1 only is correct

Section B: Structured questions

1 A fuel cell is illustrated in the diagram below.



The common electrolyte is NaOH(aq).

a **i)** Write the two ion–electron half–equations for the changes which take place at each electrode.

ii) Calculate the cell e.m.f. under standard conditions.

iii) On the diagram, mark and label the direction of electron flow through the lamp in the external circuit.

b The electrolyte in the fuel cell can also be replaced with aqueous sulfuric acid and the hydrogen can be replaced with methane. Write the two half–equations at each electrode of this fuel cell.

c Suggest one advantage of using fuel cells as a source of energy.

d One particular type of dry cell battery has zinc and carbon electrodes. Solid manganese(IV) oxide is coated on the carbon electrode. When the dry cell is in use, MnO(OH) and OH^- are produced.

i) Write an ion–electron equation, with state symbols, for the reaction which occurs at each electrode.

ii) What mass of MnO_2 is consumed when 0.10 g of zinc is used by the cell?

2 During strenuous exercise, pyruvic acid, CH_3COCO_2H, is converted to lactic acid, $CH_3CH(OH)CO_2H$, which builds up in our muscles due to limited oxygen availability.

Such anaerobic respiration is catalysed by the enzyme lactate dehydrogenase, with concomitant conversion of NADH to NAD^+. NADH plays a key role in the production of energy through redox reactions. NADH and NAD^+ are cofactors, substances that act with and are essential to the activity of an enzyme.

(i) Write a balanced equation for anaerobic respiration. Using the data given in the table below, calculate the value of $E^{\ominus}_{cell}$ for this reaction.

Electrode reaction	$E^{\ominus}$ /V
$2e^- + H^+ + NAD^+ \rightleftharpoons NADH$	–0.32
$2e^- + 2H^+ + CH_3COCOOH \rightleftharpoons CH_3CH(OH)CO_2H$	+0.89

(ii) It is not possible to use $E^{\ominus}$ values reliably to decide whether a chemical reaction will occur. Suggest a reason for this.

(iii) The activity of lactate dehydrogenase hinges on the active site Fe^{2+} contained in a heme group which can be oxidised to Fe^{3+}. Suggest a mechanism for the catalysis of anaerobic respiration by lactate dehydrogenase. Support your answers with relevant $E^{\ominus}$ values given above and from the *Data Booklet*.
You may represent the reduced and oxidised forms of the enzyme as LDH–Fe^{2+} and LDH–Fe^{3+}.

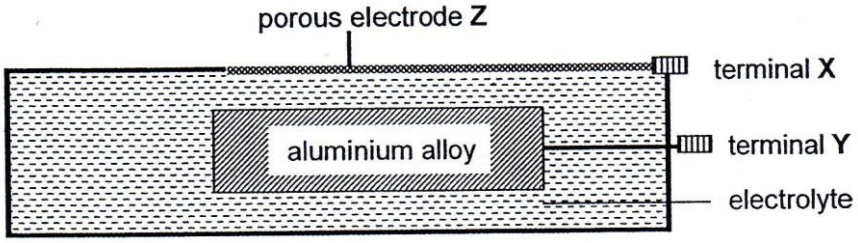
(iv) After exercising, we do not stop panting immediately because we need to breathe in additional oxygen so that lactic acid can be reconverted back to pyruvic acid. Both breathing and heart rates increase until the excess lactic acid level normalizes.

Write a balanced equation for the conversion of lactic acid back to pyruvic acid.

Calculate the value of $E^{\ominus}_{cell}$ for this reaction, with the help of the *Data Booklet*.

[8]

3 Aluminium / air batteries are used as back–up power supplies in many telephone exchanges. The structure of one such battery is shown below:



The electrolyte used is aqueous potassium hydroxide. In the reaction, oxygen in air is reduced while aluminium is oxidised as shown by the following equation:

$$Al(s) + 4OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq) + 3e^-$$

(a) Is terminal **Y** negative or positive? Give a reason for your answer. [2]

(b) Write a balanced equation with state symbols for the reaction that takes place at the porous electrode **Z**. [1]

(c) Why must electrode **Z** be porous? [1]

(d) Sometimes, electrode **Z** becomes clogged up such that it is no longer porous. This causes the aluminium / air battery to be potentially explosive. With the help of a suitable equation, explain why this is so. [2]

(e) The aluminium used is specially alloyed so that it is not easily oxidised by air. Explain why ordinary aluminium cannot be used. [1]

(f) Besides aluminium, zinc may also be used. Give two advantages of using aluminium rather than zinc. [2]

(g) When aqueous potassium hydroxide is replaced by aqueous sodium chloride, it is noticed that a white solid is formed around the aluminium alloy electrode.
Name the white solid and explain why it is formed.
[2]

(h) The aluminium / air battery with aqueous potassium hydroxide as an electrolyte was used as an electrical source to electroplate an article with copper. If the mass of aluminium electrode decreased by 5.4 g, calculate the mass of copper that had plated out of the solution. [2]

4 *Pseudohalogens are a family of inorganic compounds which possess chemical properties similar to the halogens. Two examples of pseudohalogens are cyanogen* $(CN)_2$ *and* thiocyanogen $(SCN)_2$.
The equations below show the standard reduction potentials of cyanogen and thiocyanogen.

$(CN)_2 + 2H^+ + 2e^- \rightleftharpoons 2HCN$ $\quad E^\ominus = +0.37$ V

$(SCN)_2 + 2e^- \rightleftharpoons 2SCN^-$ $\quad E^\ominus = +0.77$ V

(i) Use the *Data Booklet* to predict what you would expect to observe when the following solutions are mixed. Write balanced equations for any reaction that occurs.

I $(CN)_2(aq)$ and $Br_2(aq)$

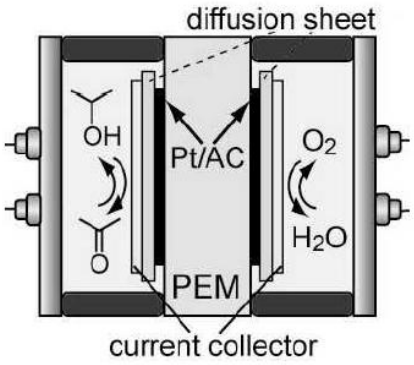
II KSCN(aq) and acidified $KMnO_4(aq)$

(ii) A reaction occurs when an unknown metal, **D**, is added to $(SCN)_2$. The standard cell potential of the reaction is determined to be +0.43 V.

Use the *Data Booklet* to deduce the identity of metal **D**, showing your working clearly.

[5]

5 In a direct propan–2–ol fuel cell (D2PFC), the electro–oxidation of propan–2–ol takes place catalytically at temperatures around 80 °C. The process produces propanone and hydrogen ions. H^+ ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water while the electrons travel through the external electrical circuit to the cathode to produce electrical power.



(a)(i) Deduce the ion–electron half–equation for the anode and hence write the overall cell reaction during discharging.

(ii) A typical D2PFC battery generates about 1.26 V.

Using the *Data Booklet*, calculate the value of $E^{\ominus}$ involving the propan–2–ol/propanone half–cell.

(iii) Explain qualitatively the change in the overall $E^{\ominus}_{cell}$ value measured when a small amount of a base is added to the propan–2–ol/propanone half–cell.

(iv) Suggest one disadvantage of using this fuel cell.

[6]

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process consists of a solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolyte cell.

(i) Suggest the half–equation including state symbols for the cathode reaction.
State an observation.

(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current of 3.5 x 10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[4]

6

(a) What is meant by the term *standard electrode potential*, SEP?

.....

.....

[2]

(b) Draw a fully labelled diagram of the apparatus you could use to measure the SEP of the Fe^{3+}/Fe^{2+} electrode.

[3]

(c) The reaction between Fe^{3+} ions and I^- ions is an equilibrium reaction.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

(i) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction.

.....

(ii) Hence state, with a reason, whether there will be more products or more reactants at equilibrium.

.....

.....

(iii) Write the expression for K_c for this reaction, and state its units.

K_c =

units .....

An experiment was carried out using solutions of $Fe^{3+}(aq)$ and $I^-(aq)$ of equal concentrations. 100 cm^3 of each solution were mixed together, and allowed to reach equilibrium.

The concentrations at equilibrium of $Fe^{3+}(aq)$ and $I_2(aq)$ were as follows.

$$[Fe^{3+}(aq)] = 2.0 \times 10^{-4}\ mol\ dm^{-3}$$
$$[I_2(aq)] = 1.0 \times 10^{-2}\ mol\ dm^{-3}$$

(iv) Use these data, together with the equation given in **(c)**, to calculate the concentrations of $Fe^{2+}(aq)$ and $I^-(aq)$ at equilibrium.

(v) Calculate the K_c for this reaction.

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7 **(i)** With reference to the *Data Booklet*, draw a fully labelled diagram showing how you could measure the standard electrode potential for the Ag^+/Ag system. Indicate the direction of electron flow.
[2]

(ii) The electrode potential, E and the concentration of silver ions in solution under non-standard conditions are related by the following equation.

$$E = 0.80 - 0.03 \lg \frac{1}{[Ag^+]^2} \quad [6]$$

The solubility product constant of AgC*l* is K_{sp} = 1.8 × 10^{-10} $mol^2\ dm^{-6}$. Using the equation given above, calculate the electrode potential at 298 K of a half-cell formed by

(I) a Ag electrode immersed in a saturated solution of AgC*l*.
(II) a Ag electrode immersed in a 0.5 mol dm^{-3} solution of KC*l* containing some AgC*l* precipitate. [5]

[3]

(iii) A cell is made by connecting the half-cell in **(d)(i)** to a standard Cu^{2+}/Cu half-cell. By reference to relevant data from the Data Booklet, calculate the cell emf and write an equation (with state symbols) for the reaction that has occurred.
[2]

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8 An electrochemical cell is composed of two half–cells, namely the AgBr | Ag and Ag^+ | Ag half–cells at 298K.

$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$ $\quad E^\ominus = +0.088\ V$

(i) Using the data booklet and the half-equation of AgBr | Ag above, write the overall equation for the cell reaction and calculate the $E^\ominus_{cell}$. [2]

(ii) The Nernst equation is used to calculate the voltage, E_{cell}, generated under non–standard conditions.

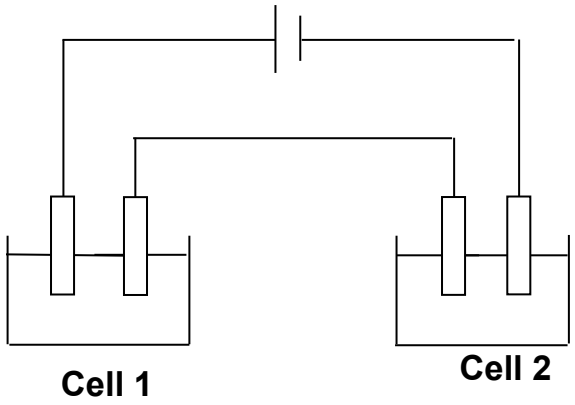
$$E_{cell} = E^\ominus_{cell} - \frac{RT}{zF} \ln 1/K_{sp}$$

Where n is the number of moles of electrons transferred per mole of equation, R is the molar gas constant, F is the Faraday constant and K_{sp} is the solubility product of AgBr.

When $E_{cell} = 0$, the system has achieved equilibrium.
Use your answer in **e(i)** and the Nernst equation to calculate the solubility product of AgBr at 298 K, stating its units.

(B) Electrolytic Cells

1



Which statements ***cannot*** be deduced from the diagram above?

A Corrosion occurs at the anode of **cell 1**.

B The anode of **cell 2** dissolves.

C The standard cell potential produced is 1.32 V.

D The electrolyte in **cell 1** increases in concentration as electrolysis proceeds.

2 When a dilute solution of the sulfate of a metal **J** is electrolysed, metal **J** and a diatomic gas **K** are produced at the cathode and the anode respectively in the molar ratio 2:1.

In another experiment, the same quantity of electricity is used to electrolyse a saturated sodium chloride solution and a gas **L** is evolved at the anode.
What is the molar ratio of **J : K : L**?

A 2 : 1 : 1 **B** 2 : 1 : 2 **C** 4 : 2 : 1 **D** 4 : 2 : 3

3 A current was passed through two cells connected in series. The first cell contained molten sodium chloride while the other contained a molten aluminium salt.
If 4.6 g of sodium was liberated from the first cell, the mass of aluminium liberated from the other cell would be

A 0.9 g **B** 1.8 g **C** 2.7 g **D** 3.6 g

4 *Use of the Data Booklet is relevant to this question.*

An antique car bumper is to be chrome–plated. The bumper is dipped into an acidic $Cr_2O_7^{2-}$ solution where it serves as an electrode of an electrolytic cell. Oxygen is formed on the other electrode.

Which statement is correct?

A The bumper is the anode of the electrolytic cell.

B Reduction of water to form oxygen occurs.

C For every 52 g of chromium plated, 3 mole of oxygen is evolved.

D It takes about 16 hours to plate 52 g of chromium if the current used is 10 A.

5 In an electrolysis that used platinum as the electrodes, a current of 2.0 A was passed through a solution of potassium sulfate. Then an excess of KI(aq) was added to the solution. The iodine evolved required 22.50 cm^3 of 0.20 mol dm^{-3} thiosulfate solution for complete reaction. The reactions involved are as follow:

$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e$

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

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

What is the time taken, in seconds, for the above electrolysis?

A 54 **B** 109 **C** 217 **D** 434

6 Two cells, one containing a molten chloride of manganese and the other containing molten chromium(III) chloride were connected in series. 33.0 g of manganese and 20.8 g of chromium were liberated.

What is the oxidation state of manganese ion in the chloride?

A +2 **B** +3 **C** +4 **D** +5

7 In an attempt to determine a value for Avogadro constant, a current, ***I***, was passed for ***t*** s into aqueous copper(II) sulfate using two Cu electrodes of mass m_1 g each.

At the end of the experiment, the mass of Cu anode was found to be m_2 g. The charge on one electron is *e* C.

What is the value for Avogadro constant, L?

A $L = \dfrac{63.5 \times I \times t}{2 \times e \times (m_1 - m_2)}$ **B** $L = \dfrac{63.5 \times I \times t}{e \times (m_2 - m_1)}$

C $L = \dfrac{2 \times e \times (m_1 - m_2)}{63.5 \times I \times t}$ **D** $L = \dfrac{e \times (m_2 - m_1)}{63.5 \times I \times t}$

8 Electroplating is an electrolytic process of coating an object with a thin layer of metal.
Which factor will affect the mass of chromium deposited at the cathode during the process of coating chromium on utensil?

A size of the anode
B size of the cathode
C size of the current
D concentration of the electrolyte

9 Which is true regarding electrolysis?

A Electrons flow from the cathode to the anode through the external circuit.
B Electricity is conducted through the electrolyte by electrons.
C The ease of discharge of metallic cations is inversely proportional to the reactivity of the metals.
D The amount of substances produced during electrolysis is directly proportional to the amount of electric current and the charge on the ions.

10 In the electrolysis of a solution of the nitrate metal **X**, 0.76 g of the element was formed at the cathode by the passage of 0.5 A of current for 1930 seconds. Metal **X** has a relative atomic mass of 152.
Which statements about the above electrolysis are correct?

1 The charge on an ion of **X** is $\frac{0.5\times1930\times152}{96500\times0.76}$ C.
2 When the gas at the anode was collected and a lighted splinter inserted into it, it burst into flame
3 The mass of **X** obtained in 1930 s can be increased by using a more concentrated solution of nitrate of metal X.

A **1, 2** and **3** are correct
B **1** and **2** are correct
C **2** and 3 are correct
D **1** only is correct

11 The discharge at the cathode of 1.00 mol of rhodium ions from aqueous solution of a rhodium salt requires 2.90 x 10^5 C of electricity.

Which conclusions can be drawn from the information?

1 The rhodium ions are positively charged.

2 The magnitude of the charge on the rhodium ions is three times the charge of an electron.

3 Rhodium is a transition element.

A **1, 2** and **3** are correct

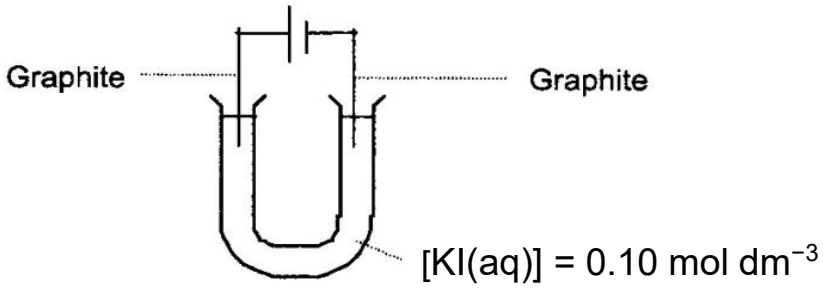
B **1** and **2** are correct

C **2** and 3 are correct

D **1** only is correct

Structured questions

1 An electrolytic cell is shown below. The U–shaped tube contains KI solution with a few drops of phenolphthalein added and is maintained at 25 ^oC.

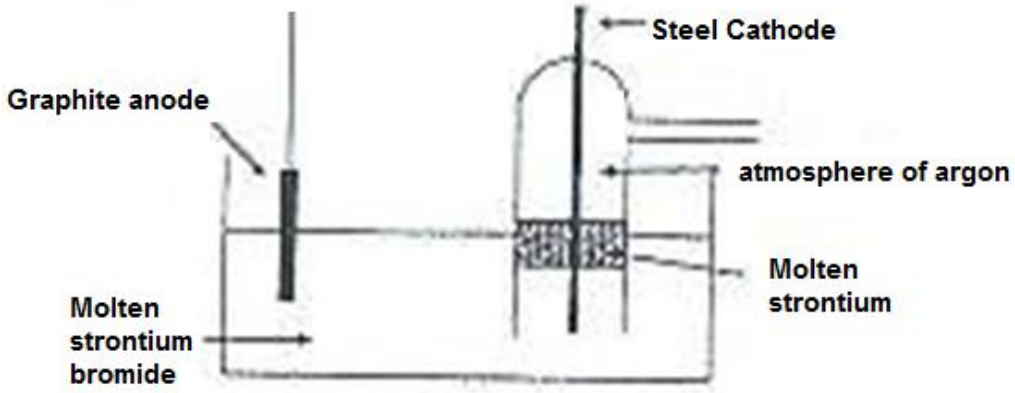


a Write the half–equation for the reaction occurring at the anode and at the cathode and state the observations.

b Using information from the *Data Booklet*, predict the minimum external voltage required for electrolysis to occur.

c Suggest what will be observed at both the electrodes when the anode is replaced with Pb.

2 Strontium metal can be obtained by the electrolysis of molten strontium bromide using the apparatus shown below:



a Write the equations, including state symbols, for the reactions which occur at the two electrodes.

b Explain why an atmosphere of argon is used around the cathode.

c How long would a current of 25.0 A have to be passed through the molten strontium bromide in order for 1 kg of strontium to be formed?

d Explain why aqueous strontium bromide cannot be used to extract strontium by electrolysis.

3 (a) Sulfuric acid is a common electrolyte used in energy cells such as in the following rechargeable cell set–up.

$$Pt(s) \mid H_2SO_4(aq) \parallel AgNO_3(aq) \mid Pt(s)$$

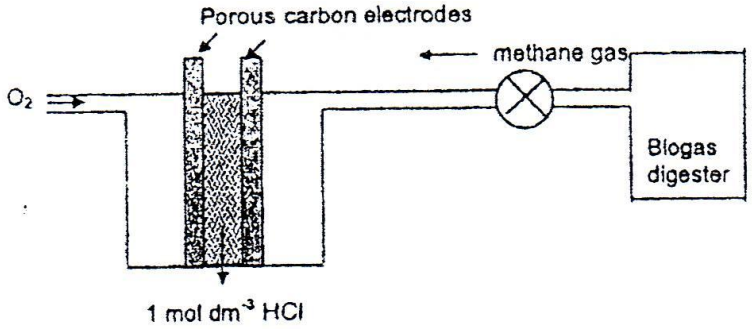
The cell was connected to an external power supply during charging.
After 2 hours, 0.0104 dm^3 of colourless and odourless gas was collected at the anode at standard conditions.

(i) Write an equation for the reaction taking place at the anode during charging. [1]

(ii) Assuming a constant current is supplied throughout, what must have been the magnitude of the current used during charging? [3]

(C) Electrochemical and Electrolytic cells

1(a) [ACJC 2006 P3] In view of the current sky–high oil prices, it has been suggested that in the near future some homes could obtain their electricity from a fuel cell which consumes methane and oxygen in an acidic electrolyte such as hydrochloric acid.



(i) Given that methane is oxidised to carbon dioxide and oxygen is reduced to water, write the half–equations for the oxidation and reduction reactions.

(ii) State the polarity of the left hand (oxygen) electrode and write the overall balanced equation for the redox reaction occurring in this cell.

(iii) Assuming that the current drawn by a household connected to this fuel cell averages 6.0 A per day, what is the mass of methane consumed by the cell each day? [6]

(b) With reference to the Data Booklet, suggest which of the following ions, Co^{2+}, Fe^{2+}, Pb^{2+}, Sn^{2+} would convert manganese(IV) oxide to aqueous manganese(II) ions in acid solution.

Calculate the $E^{\ominus}_{cell}$ value and write a balanced equation for the reaction for one of the ions you have chosen. [2]

(c) Molybdenum is commonly used an alloy with iron, ferromolybdenum. Extremely hard and strong, even at high temperatures, this alloy is used in filament supports, as heating elements for furnaces and drill bits.

Using the data given below and any other data from the *Data Booklet*, predict, with reasons, the products of the electrolysis of aqueous molybdenum(III) sulfate using inert electrodes.

$Mo^{3+}(aq) + 3e^- \rightleftharpoons Mo(s)$ $\quad E^{\ominus} = -0.20$ V [2]

2 [NYJC 2004 P3] Chlorine dioxide is a yellowish gas at room temperature. It is explosive and reactive but can be handled at temperatures below –40 °C and pressures below 50 mbar.

$$ClO_2(g) + 4H^+(aq) + 5e^- \rightleftharpoons Cl^-(aq) + 2H_2O(l) \quad E^{\ominus} = +1.50V$$

(a) Draw a fully labeled diagram to show how you could determine the standard electrode potential of the ClO_2 /Cl^- electrode system. [2]

(b)(i) Use the *Data Booklet* to predict the reaction, if any, of chlorine dioxide in acidic solution with aqueous hydrogen peroxide. Write an equation for any reaction that occurs.

[2]

(ii) What effect would a decrease in the concentration of chlorine dioxide have on the cell potential of **b(i)**? [2]

(c) Chlorine dioxide is used as a disinfectant during water treatment. An undesirable side effect is the formation of organic chlorine compounds.

The amount of organic chlorine compound in drinking water can be measured as the *Total Organic Halide* (TOX), which is expressed as mol halogen per dm^{-3} of water. *TOX* can be determined as follows.

Organic compounds are filtered out from a sample of water using activated charcoal. The charcoal is then combusted to liberate hydrogen halides:

$$\text{organic halide (RX)} \xrightarrow{O_2 / 800\ ^\circ C} CO_2 + H_2O + HX$$

The HX liberated is dissolved in water. An electrolytic cell with silver anode and platinum cathode is then used to determine the amount of halides in solution. The electrolysis stops when all the halides have precipitated. The reaction can be summarised as follows:

$$X^-(aq) + Ag(s) \rightarrow AgX(s) + e$$

(i) Write an equation for the reaction occurring at the anode, giving state symbols. [1]

(ii) When 1.0 dm^3 of drinking water was analysed, the electrolytic cell produced required a current of 4.23×10^{-3} A running for 381 s.

Assuming all the halogen is present as chlorine, calculate the *TOX* of the drinking water.

[2]

(iii) Suggest the identity of the product at the cathode. [1]

3 [HCI 2012] In 2011, scientists at Stanford University discovered a new method of generating electrical energy. The method uses a device that consists of a silver electrode coated with solid silver chloride and a porous sodium manganese manganate electrode ($Na_2Mn_5O_{10}$).

The operation of the device involves a charging and a discharging phase.

During the charging phase, the electrodes are first dipped in a tank of fresh water and a charging current is passed through.

At the anode, sodium ions are released into the freshwater through the following reaction, where MnO_2 remains on the anode.

$$Na_2Mn_5O_{10}(s) \rightarrow 2Na^+(aq) + 5MnO_2(s) + 2e$$

At the cathode, chloride ions from the solid silver chloride are released into the freshwater and silver remains on the cathode.

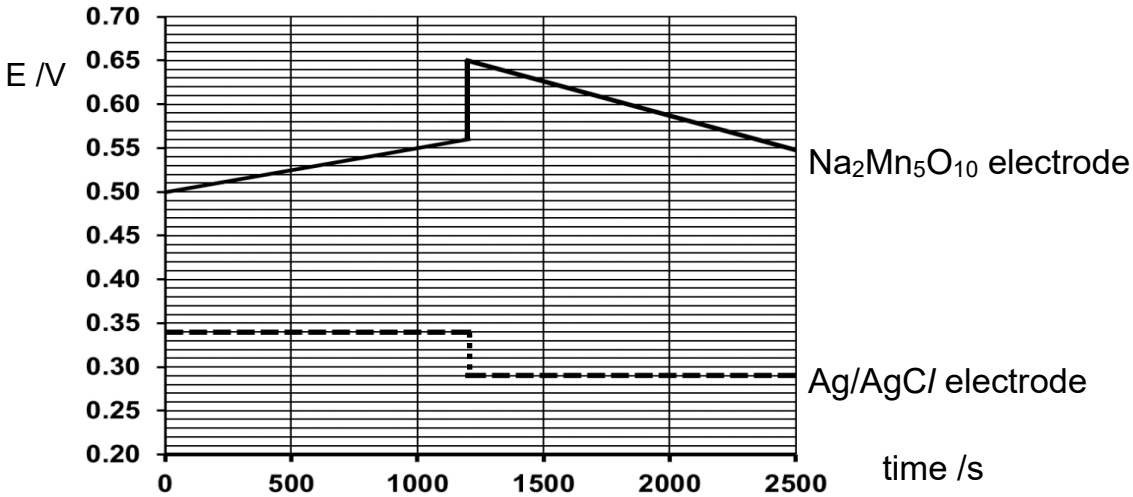
(i) Write balanced equations for the reaction that occurs at the cathode, and the overall reaction during the charging phase.

(ii) During the charging phase, the mass of the anode was reduced by 5.0 g. Calculate the quantity of charge that was used in the process.

The device can now do work by switching to the discharge phase. The charging current is stopped and the freshwater (0.024 mol dm^{-3} NaC*l*) is removed from the tank and replaced with seawater (0.600 mol dm^{-3} NaC*l*). The cell is now ready to be discharged.

(iii) Draw a labelled diagram of the electrochemical cell when it is ready to be discharged, indicating the polarity of the electrodes.

The electrode potential of each electrode was measured against a standard hydrogen electrode at various times during the operation of the device and the following graph was plotted. The device was switched from the charging to discharge phase at time = 1200 s.



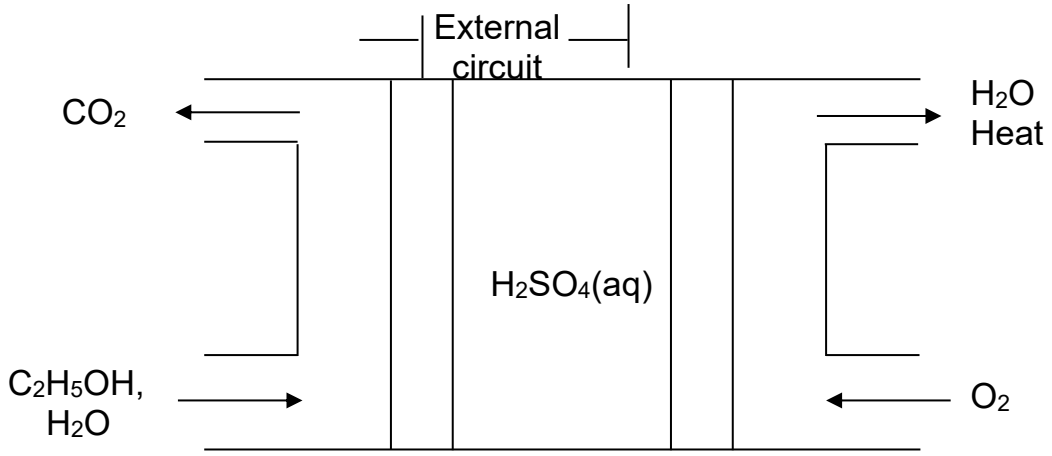
(iv) With the aid of suitable equations, explain how the replacement by seawater results in the sudden changes in potentials of each electrode.

(v) Determine the increase in cell potential during the switch from the charging to discharge phase.

[9]

4 [TJC 2013 P3] A fuel cell is an electrochemical cell that converts a fuel into electrical energy. The direct oxidation of alcohols in a fuel cell has been proven to be an efficient method of obtaining electrical energy.

(a) The diagram below illustrates the functional parts of a direct–ethanol fuel cell (DEFC).



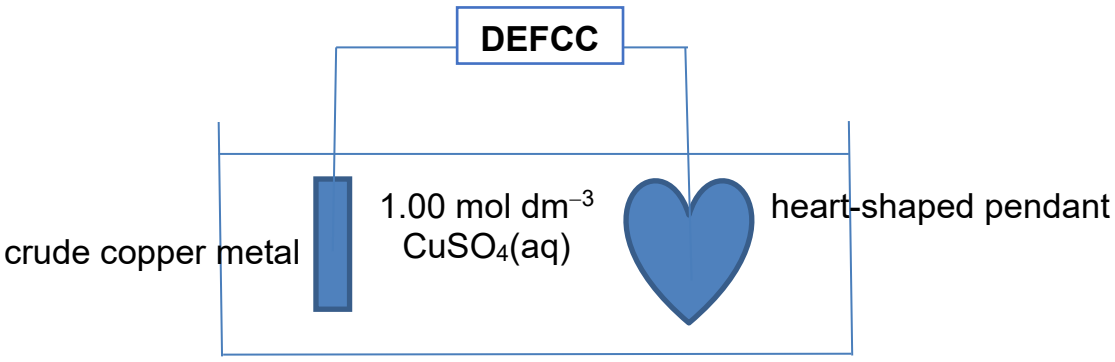
(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

(ii) The cell is capable of producing an e.m.f. of 1.61 V. By using suitable data from the *Data Booklet*, suggest a value for the E^{θ} of the CO_2/C_2H_5OH electrode reaction.

(iii) The first alcohol to be used successfully in a fuel cell was not ethanol but methanol. Suggest a possible advantage of using ethanol compared to methanol as fuel.

[5]

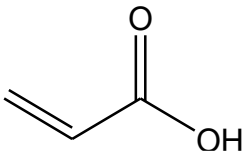
(b) In an attempt to coat a heart–shaped pendant with copper in the laboratory, a researcher connected the DEFC to an electrolytic cell as shown below.



(i) Calculate the volume of $CO_2(g)$ produced by the DEFC when 31.75 g of copper metal was plated onto the pendant at room conditions.

(ii) The total time taken for the 31.75 g of copper to be plated was 8 hours. Calculate the current produced by the DEFC. [4]

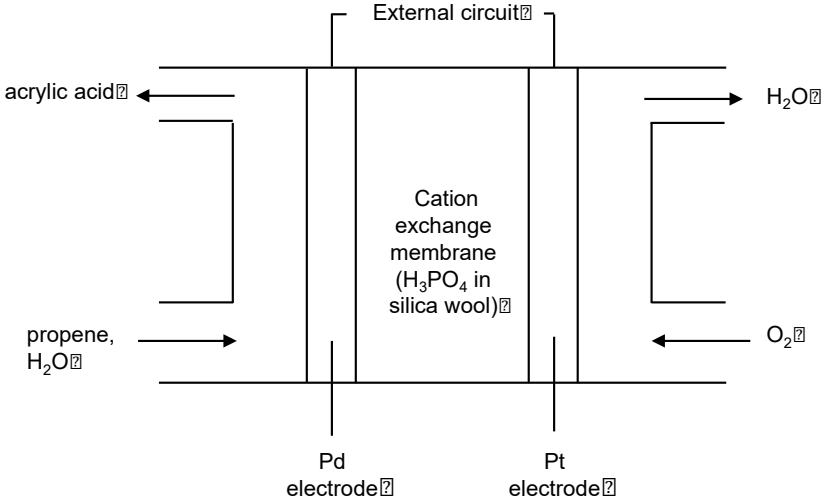
5. (modified from NYJC 2015/P3/Q2)
Acrylic acid is used in the manufacture of a large variety of plastics, paint formulations, and polymer coatings. More than 1000 kilotonnes of acrylic acid are produced for industrial use in a year.



acrylic acid

(a) A method of synthesising acrylic acid is by reacting propene and steam with Pd catalyst in a fuel cell. Pd acts as both an electrode and a catalyst in the fuel cell.

Propene is pumped in at the Pd electrode, while air (as a source of oxygen) is pumped in at the Pt electrode. The cell is operated in the gas phase at 365 K and atmospheric pressure. Electricity is generated during the reaction, making the process economically viable.



(i) Write half–equations for the reactions occurring at the cathode and the anode in the fuel cell. State the polarities of each electrode.

(ii) The fuel cell is capable of producing an E_{cell} of +0.70 V under the conditions of operation. Given that the electrode potential of the acrylic acid/propene half cell is +0.53 V under these conditions, calculate the electrode potential of the O_2/H_2O half cell under the same conditions.

(iii) With reference to your answer in **(ii)** and the Data Booklet, use Le Chatelier's Principle to determine if the operation temperature of the fuel cell should be increased. [6]

(b) The electricity generated by the fuel cell during the reaction was used to electroplate silica disks with Pt as part of the manufacture of new fuel cells. The electrolyte used was a solution of $[Pt(NH_3)_4]^{2+}$ (aq).

(i) Draw a diagram to illustrate the electroplating set–up. You can use a battery symbol (–| –) to represent the fuel cell.

(ii) The $[Pt(NH_3)_4]^{2+}$ complex reacts to form platinum metal during the electroplating process. Write a half–equation for this reaction.

(iii) Suggest with reason, a value for $E([Pt(NH_3)_4]^{2+}/Pt)$.

(iv) A silica disk of surface area 2.00 cm^2 was coated with a 0.40 cm thick layer of Pt. Calculate the mass of acrylic acid generated from the fuel cell during this plating process. (Density of Pt is 21.5 g cm^{-3}) [6]

Answers. Electrochemistry

(A) Electrochemical Cells

MCQ

1	**C**	**D**	**C**	**B**	**D**	**6**	**C**	**D**	**B**	**C**	**B**
11	**B**	**D**	**A**	**A**							

Worked solution for MCQ:

1 Since $E^{\theta}_{Y+/Y}$ more positive than $E^{\theta}_{X2+/X}$, Y^{2+}/Y half cell undergoes reduction and the X^{2+}/X half cell undergoes oxidation. Hence electron flows from electrode X (Anode as it undergoes oxidation = loss of electrons) to electrode Y (cathode – gain of electrons).
$E^{\theta}_{cell} = E^{\theta}_{Y+/Y} – E^{\theta}_{(X2+/X)} = +0.80 – (–0.25) = +1.05V$

Since oxidation takes place at the X^{2+}/X half cell, it means that the electrode X is oxidized to X^{2+}, which enters the solution forming $X^{2+}(aq)$.

2 Sb_2O_5 is found on the LHS of a half equation (E_4), while $S_2O_3^{2–}$ is found on the RHS of another half equation (E_1), this means that Sb_2O_5 is reduced while $S_2O_3^{2–}$ is oxidized. Since a redox reaction happens between Sb_2O_5 and $S_2O_3^{2–}$ => $E_{cell} > 0$. $E_4 – E_1 > 0$, hence $E_4 > E_1$.

Sb_2O_5 is found on the LHS of a half equation (E_4) and Hg is found on the RHS of another half equation(E_3), this means that Sb_2O_5 could have been reduced while Hg could have been oxidized. Since no reaction occurs between Sb_2O_5 and Hg when mixed, $E_{cell} < 0$. $E_4 – E_3 < 0$. Hence $E_3 > E_4$.
$[SnCl_6]^{2–}$ is found on the LHS of a half equation (E_2) and $S_2O_3^{2–}$ is found on the RHS of another half equation (E_1), this means that $[SnCl_6]^{2–}$ could have been reduced while $S_2O_3^{2–}$ could have been oxidized. Since no reaction occurs between $[SnCl_6]^{2–}$ and $S_2O_3^{2–}$, $E_{cell} < 0$. $E_2 – E_1 < 0$. Hence $E_1 > E_2$.
Conclusion: $E_3 > E_4 > E_1 > E_2$

3 Arranging from weakest RA to strongest RA means arranging from **lowest tendency to be oxidized to highest tendency to be oxidized**.
Metal X and Y are oxidized while Cu^{2+}/Cu half–cell undergoes reduction since metal X and Y are negative electrodes when connected to Cu. Hence both metals X and Y are stronger reducing agent than Cu. Since the emf between metal Y and Cu (1.10V) >

emf between metal X and Cu (0.45V), E_{ox} of Y is more positive than E_{ox} of X. Y has a stronger reducing strength than X.

Z^{2+}/Z half–cell is reduced while Cu is oxidized. Since metal Z is the positive electrode when connected to copper. Hence Cu have a higher tendency to be oxidized thus is stronger reducing agent than metal Z.

Hence tendency to be oxidized : Z < Cu < X < Y

2 A: Adding water to the Fe^{3+}/Fe^{2+} half cell will decrease the $[Fe^{3+}]$ and $[Fe^{2+}]$ by the same extent, ratio of $\frac{[Fe^{2+}]}{[Fe^{3+}]}$ remains unchanged, hence no shift in eqm and no change in $E^{\theta}_{Fe3+/Fe2+}$ and hence no change in E^{θ}_{cell}.

B :From the Data booklet, $E^{\theta}_{Mg2+/Mg} = -2.38V$ and $E^{\theta}_{Fe3+/Fe2+} = +0.77V$.
Hence reaction taking place at the Mg electrode is oxidation: $Mg \rightarrow Mg^{2+} + 2e$.
Adding NaOH will precipitate Mg^{2+} and hence reducing $[Mg^{2+}]$, favouring the oxidation process, increasing $E_{ox\ Mg\ /Mg2+}$, resulting in E_{cell} or emf increasing since $E_{cell} = E_{Fe3+/Fe2+} - E_{Mg2+/\ Mg}$

C: Increasing the temperature will affect the position of both half cell eqm to different extent and change the electrode potential values of each half cells and will hence change the E_{cell} value.

D: Since $E^{\theta}_{Mg2+/Mg}$ more negative than $E^{\theta}_{Fe3+/Fe2+}$, the Mg^{2+}/Mg half cell undergoes oxidation and electrons would be flowing out of the Mg electrode (oxidation is loss of electron), and hence the Mg electrode is the negative electrode

5 Any factors that causes eqm to shift right will help the reaction to proceed.

A: eqm shifts right to partially offset the increase in $[H^+]$ by reacting H^+ away, thus helping forward reaction to proceed.

B: eqm shifts right to partially offset the increase in $[NO_3^-]$ (potassium nitrate is fully soluble in water) by reacting the NO_3^- ion away. Thus helping the forward reaction to proceed.

C: KI reduces $Cl_2(g)$ to Cl^-. Eqm shifts right to partially offset the reduction in $[Cl_2]$ by producing more Cl_2, thus helping the forward reaction to proceed.

D: Bromine does not react with any of the reactants or product in the eqn,

i.e. conc of reactants and products remain unchanged. Position of eqm not affected and does not help the reaction to proceed.

6. Decreasing reducing power means decreasing tendency to be oxidized.
In an electrochemical cell, oxidation takes place at the negative electrode (since oxidation is loss of electron and electrons flow out of a negative electrode).
Mg is oxidized while metals A and B half–cells are reduced.
➔ Mg has a higher reducing power than metals A and B. Since the emf between B and Mg (+2.72V) is larger than that between A and Mg (+2.10V), Metal B has a more positive reduction potential than A.
➔ B has a weaker reducing power than A.
➔ Metal C is oxidized while Mg^{2+}/Mg half–cell is reduced. Hence C has a stronger reducing power than Mg.
Hence decreasing tendency to be oxidized: C > Mg > A > B

7. From the Data Booklet $E^{\theta}_{Fe3+/Fe2+} = +0.77V$ and $E^{\theta}_{Ni2+/Ni} = –0.25V$.
A: Since $E^{\theta}_{Fe3+/Fe2+}$ is more positive than $E^{\theta}_{Ni2+/Ni}$, reduction takes place at the Fe^{3+}/Fe^{2+} half–cell and the half–cell turns green as more Fe^{2+} are formed from the reduction of Fe^{3+}.
B: Standard cell potential = $E^{\theta}_{Fe3+/Fe2+} – E^{\theta}_{Ni2+/Ni}$
$= 0.77 – (–0.25) = +1.02V$
C: Electrons flow from the half cell that is oxidized (Ni^{2+}/Ni) to the half cell that is reduced (Fe^{3+}/Fe^{2+}).
D: Cathode is the electrode where reduction takes place (recall RED CAT), which is the Fe^{3+}/Fe^{2+} half–cell. Hence the mass of metal cathode should remain unchanged as Fe^{3+} is reduced to Fe^{2+}.

8. From the Data booklet, $E^{\theta}_{Cr2O72–/Cr3+} = +1.33$ V, $E^{\theta}_{MnO4–/Mn2+} = +1.52V$.
$Cr_2O_7^{2–}/Cr^{3+}$ half cell undergoes oxidation while $MnO_4^–/Mn^{2+}$ half cell undergoes reduction. Hence $E^{\theta}_{cell} = E^{\theta}_{MnO4–/Mn2+} – E^{\theta}_{Cr2O72–/Cr3+}$
A Adding a reagent that complexes with Mn^{2+} decreases $[Mn^{2+}]$. Reduction of $MnO_4^–$ is favoured to partially offset the reduction in $[Mn^{2+}]$ by forming more Mn^{2+}. This increases $E_{MnO4–/Mn2+}$ and hence increases E_{cell} (Cell potential)
B Oxidation of Mn^{2+} is favoured to partially offset the increase in $[Mn^{2+}]$ by reacting Mn^{2+} away. This decreases $E_{MnO4–/Mn2+}$ and hence decreases E_{cell} (Cell potential)

C Changing the electrode to Mn is not a continuous change and does not result in continual decrease in cell potential measured.

D Adding more acid to the MnO_4^-/Mn^{2+} half cell increases $[H^+]$. Reduction of MnO_4^- is favoured to partially offset increase in $[H^+]$ by reacting H^+ away.
$E_{MnO4-/Mn2+}$ increases resulting in an increase in the E_{cell} (Cell potential)

9. From cell notation, Fe^{2+}/Fe half cell undergoes oxidation, while Ni^{2+}/Ni half cell undergoes reduction. Hence E^{θ}_{cell} (cell potential) = $E^{\theta}_{Ni2+/Ni} - E^{\theta}_{Fe2+/Fe}$

A Adding nickel(II) chloride increase $[Ni^{2+}]$, hence reduction of Ni^{2+} is favoured to partially offset the increase in $[Ni^{2+}]$ by reacting Ni^{2+} away. $E_{Ni2+/Ni}$ increase, which results in an increase in E_{cell} (cell potential).

B Adding aqueous cyanide ions to iron half cell will decrease $[Fe^{2+}]$ since cyanide forms complex with Fe^{2+}. Hence oxidation of Fe is favoured to partially offset the reduction in $[Fe^{2+}]$ by forming more Fe^{2+}, Eox increases,
$\therefore$ increase in E_{cell} (cell potential).

C Adding water to the nickel half cell decrease the $[Ni^{2+}]$. Oxidation of Ni is favoured to partially offset reduction in $[Ni^{2+}]$ by forming more Ni^{2+}.
$\therefore E_{Ni2+/Ni}$ decrease, which results in a decrease in E_{cell} (cell potential).

D increasing the surface area of iron does not affect position of eqm .
no effect on $E^{\theta}_{Fe2+/Fe}$ and E^{θ}_{cell} (cell potential) values.

10. A: Increasing size of electrode has no effect on position of eqm and hence no change in cell potential.
B: Since 15 ^oC is the transition temperature at which white and grey tin are in eqm, there is no net current flow between both half cells.
C: Since below 15 ^oC white tin from **W** dissolves and is deposited as grey tin on **G**, the reverse is true above 15 ^oC.
i.e, grey tin from **G** dissolves (is oxidized to form Tin ions) and is deposited (tin ions is reduced back to Tin) as white tin on **W**.
Hence electrons must flow from **G** (where oxidation is taking place) to **W** (where reduction is taking place) above 15 ^oC

D: Since white tin is being deposited above 15 °C, the stable form of tin at 25 °C would be the white form.

11 1: Since $E^{\theta}_{sn2+/amalgam} > E^{\theta}_{Al3+/Al}$, Sn^{2+}/amalgam half cell undergoes reduction indicating that the electrons flows towards the amalgam, hence the amalgam is the positive electrode.

2: Since Sn^{2+}/amalgam half cell is being reduced, this means that there must be small amount of Sn^{2+} to receive the incoming electrons to be reduced to Sn.

3: Standard cell potential involving aluminium foil

$= E^{\theta}_{Al3+/Al} - E^{\theta}_{sn2+/amalgam} = -0.13 - (-1.66) = +1.53$ V

Standard cell potential involving stainless steel

$= E^{\theta}_{Fe2+/Fe} - E^{\theta}_{sn2+/amalgam} = -0.13 - (-0.44) = +0.31$ V

Hence, standard cell potential involving Al foil is larger.

12 1: Since $E^{\theta}_{P+/P} > E^{\theta}_{Q2+/Q}$, $E^{\theta}_{cell} = E^{\theta}_{P+/P} - E^{\theta}_{Q2+/Q} = +1.80 - (+0.3) = 1.50$ V

2: $E^{\theta}_{cell} = E^{\theta}_{[R]} - E^{\theta}_{[O]} = E^{\theta}_{R+/R} - E^{\theta}_{S2+/S}$. Since $E^{\theta}_{R+/R} < E^{\theta}_{S2+/S}$, $E^{\theta}_{cell} < 0$, and rxn is not spontaneous. Hence S could not be oxidized by R^{+}

3: P^{+} is of the higher oxidation state than P in the P^{+}/P half cell, hence P^{+} can only be reduced and be an oxidizing agent. It is not a reducing agent.

13 1: Since $E^{\theta}_{MnO4-/Mn2+}$ is more positive than $E^{\theta}_{I2/I-}$,

$E^{\theta}_{cell} = E^{\theta}_{MnO4-/Mn2+} - E^{\theta}_{I2/I-} = +1.52 - (+0.54) = 0.98$ V

2: I_2/ I^{-} half cell undergoes oxidation, where I^{-} is oxidized to brown I_2. Hence KI solution turns brown.

3: Since $E^{\theta}_{MnO4-/Mn2+} > E^{\theta}_{I2/I-}$, MnO_4^{-}/Mn^{2+} half cell undergoes reduction, where purple MnO_4^{-} is reduced to colourless Mn^{2+}.

➔ Hence purple $KMnO_4$ solution becomes less intense.

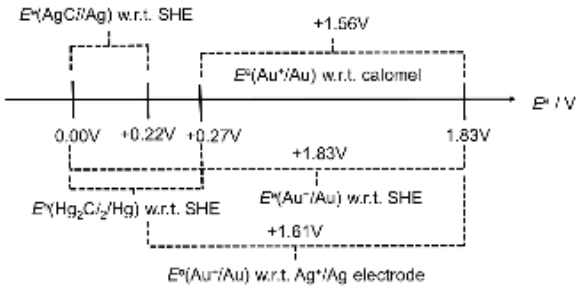
14 1: Since $E^{\theta}_{Co2+/Co}$ more positive than $E^{\theta}_{Ga3+/Ga}$, Co^{2+} has a higher tendency to be reduced compared to Ga^{3+} . Co^{2+} is a stronger oxidizing agent than Ga^{3+}.

2: Since $E^{\theta}_{In3+/In}$ is more positive than $E^{\theta}_{Cd2+/Cd}$, In has a lower tendency to be oxidized compared to Cd. In is a weaker reducing agent than Cd.

3: Since $E^{\theta}_{Co3+/Co2+}$ is more positive than $E^{\theta}_{In3+/In}$, Co^{3+} can be reduced to Co^{2+} by In;

Since $E^{\theta}_{Co2+/Co}$ more positive than $E^{\theta}_{In3+/In}$, Co^{2+} formed can be further reduced to Co by In. Hence in total, Co^{3+} can be reduced to Co by In.

15 **A**



Option **A**: $E^{\circ}(Au^{+}/Au)$ wrt the SHE = +1.56 + (+0.27) = +1.83 V (refer to diagram above)
Option **B**: $E^{\circ}(Au^{+}/Au)$ wrt the AgCl/Ag electrode = +1.56 + (0.27 – 0.22) = +1.61 V (refer to diagram above)
Option **C**: The reduction potential of AgCl/Ag half–cell (+0.22 V) is more positive than that of H^{+}/H_2 half–cell (0.00 V). Hence Ag has a lower tendency to be oxidised than H_2.
Option **D**: The reduction potential of Hg_2Cl_2/Hg half–cell (+0.27 V) is more positive than that of AgCl/Ag half–cell (+0.22 V). Hence Hg_2Cl_2 has a higher tendency to be reduced than AgCl.

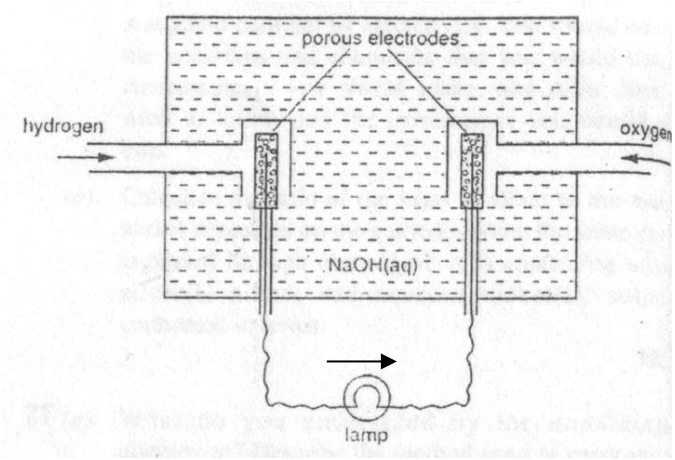
16 **A (1, 2 and 3 are correct)**
Option **1**: Correct
$NaBO_2 + 6H_2O + 8e^- \rightleftharpoons NaBH_4 + 8OH^-$ $E^{\circ} = -1.24$ V
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $E^{\circ} = +0.40$ V
$E^{\circ}_{cell} = 0.40 - (-1.24) = +1.64$ V
Option **2**: Correct
$NaBH_4$ is oxidised to $NaBO_2$ at the anode **X** while O_2 is reduced to OH^- at the cathode **Y**.
Option **3**: Correct
The BO_2^- anion has 2 bond pairs and 0 lone pair around the central B atom, giving it a linear shape with a bond angle of 180°.

Structured

1 **a** **i)** Anode [O]: $H_2 + 2OH^- \rightarrow 2H_2O + 2e$

Cathode [R]: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

ii) $E^{o}_{cell} = +0.83 - (-0.40) = +1.23$ V



Electrons flow from left electrode to the right electrode through external circuit

b CH_4 is oxidised to CO_2 (just construct this eqn by following the rules of balancing redox half–eqn, in acidic medium)

At negative electrode [O]: $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e$

At postive electrode [R]: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

Overall: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

c Does not produce harmful gases, no pollution

d i) Construct equations by following rules of balancing redox half–equations in alkaline medium.

At negative electrode [O]: $Zn(s) + 2\ OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e$

At postive electrode [R]: $MnO_2(s) + H_2O(l) + e \rightarrow MnO(OH)(s) + OH^-(aq)$

ii) From the balance equation,

$Zn \equiv 2MnO_2$

$$\eta_{MnO_2} = 2 \times \eta_{Zn} = \frac{0.1}{65.4} \times 2 \text{ mol}$$

$$\text{Mass of } MnO_2 = \frac{0.1}{65.4} \times 2\ (54.9 + 2 \times 16.0) = 0.266 \text{ g}$$

2(i) $CH_3COCO_2H + NADH + H^+ \rightarrow CH_3CH(OH)CO_2H + NAD^+$

$E^\ominus = +0.89 - (-0.32) = +1.21$ V **> 0** $\Rightarrow$ feasible reaction

(ii) The reaction may not be kinetically feasible due to high activation energy though it is thermodynamically feasible as indicated by a positive $E^\ominus_{cell}$ value.

(iii) Step 1: $2LDH\text{–}Fe^{2+} + CH_3COCOOH + 2H^+ \rightarrow 2LDH\text{–}Fe^{3+} + CH_3CH(OH)COOH$

$E^\ominus_{cell} = +0.89 - (+0.77) = +0.12$ V > 0 $\Rightarrow$ feasible reaction

Step 2: $2LDH\text{–}Fe^{3+} + NADH \rightarrow 2LDH\text{–}Fe^{2+} + NAD^+ + H^+$

$E^\ominus_{cell} = +0.77 - (-0.32) = +1.09$ V > 0 $\Rightarrow$ feasible reaction

(iv) $O_2 + 2CH_3CH(OH)CO_2H \rightarrow 2H_2O + 2CH_3COCO_2H$

$E^\ominus = +1.23 - (+0.89) = +0.34$ V

3(a) Terminal **Y** is negative as it is where oxidation takes place. Electrons released as a result of oxidation of Al.

(b) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

(c) **Z** must be porous so that oxygen may diffuse through the electrode and come into contact with the electrolyte where it is reduced.

(d) Instead of oxygen being reduced, water may be reduced at electrode **Z** forming hydrogen gas: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

H_2 is formed and is potentially explosive. Alternatively, gas is produced in a sealed container, so potentially explosive.

(e) Ordinary aluminium is protected by a dense, impervious layer of aluminium oxide – a non–conductor of electricity. This prevents Al from being oxidised and electrons cannot be produced.

(f)

- Al has a more negative standard reduction potential (SEP) so that the operating voltage of Al/air battery is higher than Zn/air battery.
- Al produces more electron per mole of metal so that more electrons can be produced from Al/air battery than Zn/air battery for the same mass of metal used.
- Al is less dense than Zn & hence is lighter. Can be deduced from the relative Ar of Zn and Al.

(g) Aluminium hydroxide, $Al(OH)_3$.

– insufficient hydroxide ions to dissolve $Al(OH)_3$, which is formed due to precipitation reaction between Al^{3+} (produced by oxidation of Al) and OH^- (Produced by reduction of oxygen).

(h) $Al \longrightarrow Al^{3+}(aq) + 3e$ $\quad Cu^{2+} + 2e \longrightarrow Cu$

Assume: all e released from oxidation of Al Are used to reduce Cu^{2+} to Cu

$2Al \equiv 3\ Cu$ $\quad \eta_{Cu}$ formed $= \frac{3}{2} \times \eta_{Al} = \frac{3}{2} \times \frac{5.4}{27.0}$ mol

$\therefore$ mass of Cu formed $= \frac{3}{2} \times \frac{5.4}{27.0} \times 63.5 =$ **19.1** g

4(i) **I** $(CN)_2 + 2H^+ + 2e \rightleftharpoons 2HCN$ $\quad E^\ominus = +0.37$ V

$Br_2 + 2e \rightleftharpoons 2Br^-$ $\quad E^\ominus = +1.07$ V

Orange solution remains orange; no reaction as both are oxidising agents.

II

$(SCN)_2 + 2e^- \rightleftharpoons 2SCN^-$ $\quad E^\ominus = +0.77$ V

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad E^\ominus = +1.52$ V

$E^\ominus_{cell} = (+1.52) - (+0.77) = +0.75$ V $> 0 \Rightarrow$ reaction is feasible.

$10SCN^- + 2MnO_4^- + 16H^+ \rightarrow 5(SCN)_2 + 2Mn^{2+} + 8H_2O$

Purple $KMnO_4$ would decolourise.

(ii) Reduction: $(SCN)_2 + 2e^- \rightarrow 2SCN^-$ $E^{\ominus}_{red} = +0.77$ V

$E^{\ominus}_{cell} = E^{\ominus}_{(SCN)2} - E^{\ominus}_{Z}$

$E^{\ominus}_{Z} = +0.77 - 0.43 =$ **+0.34** V

$Cu^{2+} + 2e^- \rightarrow 2Cu$ $E^{\ominus}_{red} = +0.34$ V

Hence, **D** is <u>copper</u>.

5(a)(i) $CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e$

$2CH_3CH(OH)CH_3 + O_2 \rightarrow 2CH_3COCH_3 + 2H_2O$

(ii) $E^{\ominus} = -0.03$ V

(iii) OH^- neutralises H^+, causing $[H^+]$ to decrease; oxidation of propan–2–ol is favoured to partially offset the reduction in $[H^+]$ by forming more H^+. $E^{\ominus}_{ox\ CH3CH(OH)CH3}$ will become more positive; hence, a more positive E_{cell}.

(iv) Availability of propan–2–ol as source. **Other answers possible*

(b)(i) $[Pt(NH_3)_4]^{2+}(aq) + 2e \rightarrow Pt(s) + 4NH_3(g)$. Grey solid formed or pungent ammonia gas evolved (or state test for ammonia)

(ii) No of moles of Pt formed $= \frac{1}{2} \times \eta_e = \frac{1}{2} \times \frac{It}{F}$

$$= \frac{1}{2} \times \frac{25 \times 3.5 \times 10^{-3} \times 75 \times 60}{96500} = 2.04 \times 10^{-3} \text{ mol}$$

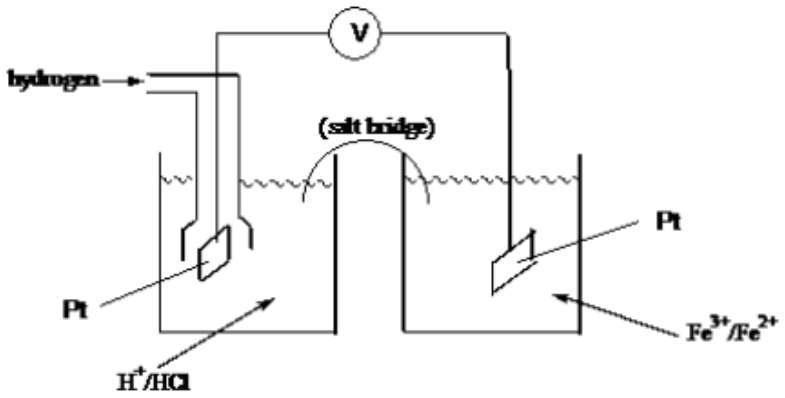
Mass of Pt formed $= 2.04 \times 10^{-3} \times 195 =$ **0.398** g

6

(a) The potential of an **electrode** compared to that of a standard hydrogen electrode (SHE)
or
the EMF of a **cell** composed of the test electrode and the SHE [1]

all measurement concentrations of 1 mol dm^{-3} **and** 298 K / 1 atm pressure [1]
[2]

(b)



H_2 and good delivery system
Fe^{2+}/Fe^{3+} solution labelled
platinum electrodes (both)
salt bridge and voltmeter
H^+ *or* HC*l* *or* H_2SO_4

(c) **(i)** $E^\ominus = 0.77 - 0.54 = 0.23$ (V) [1]

(ii) Since $E^\ominus$ is positive/ $E^\ominus > 0$

So more products / the equilibrium will be over to the right / forward reaction is favoured
ecf from **(c)(i)** [1]

(iii) $K_c = [Fe^{2+}]^2[I_2]/[Fe^{3+}]^2[I^-]^2$ [1]

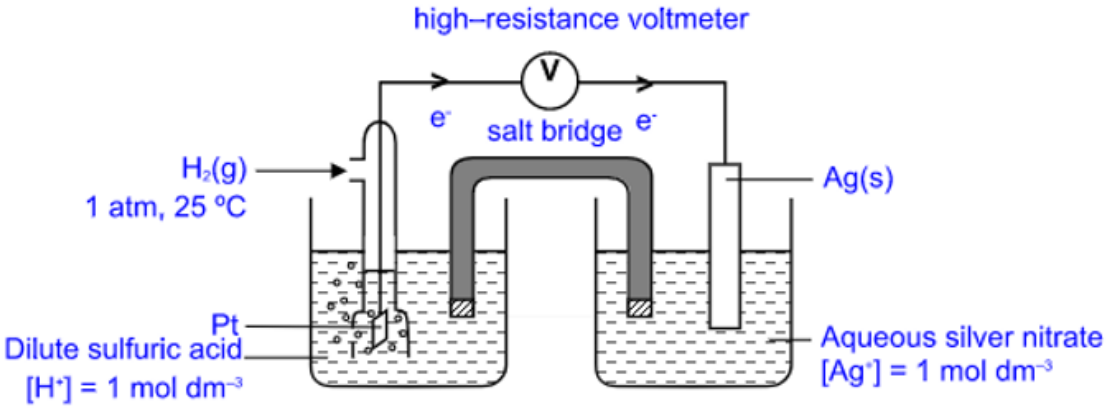
units are **mol^{-1} dm^3** ecf on expression [1]

(iv) ($[Fe^{2+}]$ must always be twice $[I_2]$, so) $[Fe^{2+}] = 0.02$ (mol dm^{-3}) [1]

($[I^-]$ must always be equal to $[Fe^{3+}]$, so) $[I^-] = 2 \times 10^{-4}$ (mol dm^{-3}) [1]

(v) $K_c = \{(0.02)^2 \times 0.01\} / \{(2 \times 10^{-4})^2 \times (2 \times 10^{-4})^2\}$ correct expression [1]
(allow ecf from incorrect expression in **(c)(iii)**)
(allow ecf from **(c)(iv)**)
$= (4 \times 10^{-6}) / (1.6 \times 10^{-1.5}) = 2.5 \times 10^9$ (mol^{-1} dm^3) [1]
[8]

7(i)



(ii)

(I) a Ag electrode immersed in a saturated solution of AgCl.

$[Ag^+] = \sqrt{1.8 \times 10^{-10}}$
$= 1.3 \times 10^{-5}$ mol dm^{-3}
$E = 0.80 - 0.03 \log$
$= +0.51$ V

(II) a Ag electrode immersed in a 0.5 mol dm^{-3} solution of KCl containing some AgCl precipitate.

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.5}$$

$= 3.6 \times 10^{-10}$ mol dm^{-3}
$E = 0.80 - 0.03 \log$
$= +0.23$ V [3]

(iii)

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V
$E_{cell} = 0.80 - 0.34$
$= +0.46$ V
Eqn: $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

8 i) **AgBr(s) + e** $\rightleftharpoons$ Ag(s) + Br^-(aq) $E^\ominus = +0.088$ V

$Ag^+ + e \rightleftharpoons Ag$ $E^\ominus = +0.8$ V

Overall eqn: $Ag^+ + Br^- \rightarrow AgBr$

$E^\ominus_{cell} = 0.8 - 0.088 = +0.712$ V

(ii)

n = 1 ;

At equilibrium, $E_{cell} = 0$ V

$0 = E^\ominus_{cell} - (RT/nF) \ln(1/K_{sp})$

Therefore, $0 = +0.712 - (8.31)(298)/(1)(96500) \ln (1/K_{sp})$

K_{sp} = **8.92 x 10^{-13} mol^2 dm^{-6}**

(B) Electrolytic Cells

MCQ

1	**C**	**B**	**B**	**D**	**C**	**6**	**A**	**A**	**C**	**C**	**B**
11	**B**										

Worked solution:

1 Anode is where oxidation occurs. Since no bubbles is observed in the diagram, no anions are oxidised at the anode to form gases, the anode itself is being oxidised. Hence the anode of both cells can be described to be "corroded" and seen to be "dissolving" into the electrolyte as time goes by.
As the anode is being oxidised to form Cations, the concentration of the electrolyte increase.
Since the identity of both cells are not given, it is not possible to deduce the standard cell potential.

2 Since the electrolyte is dilute sulfate of metal J, and sulfate anion cannot be oxidised at the anode, H_2O would be oxidised at the anode to form O_2 gas which is gas K. From Data booklet: $2H_2O \rightarrow O_2 + 4H^+ + 4e$.
Since metal J and O_2 is produced in the ratio of 2:1, J must have a charge of 2+ with half eqn given as $J^{2+} + 2e \rightarrow J$. This is such that when the half eqn is multiplied by 2, coefficient of the electron becomes 4, which can be combined with the anode half eqn, and **no of mol of J = 2**, while **no of mol of O_2 = 1**.
When electrolysing saturated sodium chloride, chlorine gas (gas L) is evolved at the anode, $2Cl^- \rightarrow Cl_2 + 2e$ ---(2).
When eqn (2) is multiplied by 2 (in order to make the coefficient of electron = 4, same as that of the other 2 half eqns), **no of mol of Cl_2 gas becomes 2**.
Hence mol ratio of J : K : L is 2 : 1 : 2

3 liberation of Na from first cell: $Na^+ + e \rightarrow Na$ ——(1)
liberation of Al from second cell: $Al^{3+} + 3e \rightarrow Al$ –(2)

Since both cells are connected in series, the same amount of current and hence the same amt of electrons must pass through both cells.
To make coefficient of electrons of both half equations the same, take eqn (1) x 3 to become: $3Na^+ + 3e \rightarrow 3Na$

Hence mol ratio of Na : Al = 3 : 1
No of mol of Na formed = $\frac{4.6}{23.0}$ = 0.2 mol

Hence no of mol of Al formed = $\frac{1}{3} \times 0.2$ = 0.0667mol

Mass of Al formed = 0.0667 x 27.0 = 1.80 g

4 A: The object to be plated should be the cathode so that metal cations can be reduced at the cathode to form metal that plates the object.

B: Since the bumper is the cathode, oxygen formed on the other electrode would be the anode.
Anode is where oxidation takes place. Hence oxidation of water to form oxygen occurs. Oxidation state of O increases from –2 in H_2O to 0 in O_2.
Hence conversion of water to oxygen must be oxidation rather than Reduction.

C: Since the oxidation state of Cr in $Cr_2O_7^{2-}$ is +6, it would take 6 moles of electrons to deposit one mol of Cr at the cathode.
$Cr^{6+} + 6e \rightarrow Cr$ ------(1).
At the anode, it would take 4 mol of electrons to form one mol of O_2.

$2H_2O \rightarrow O_2 + 4H^+ + 4e$ ----(2) (Data Booklet).
To make the coefficient of electrons same for both cathode and anode,
Equation (1) x 4 and equation (2) x 6
Hence the mole ratio of Cr : O_2
4 : 6
2 : 3
52 g of Cr = 1 mol, which should form 3/2 mol of O_2

D: using $It = n_eF$

$t = \frac{n_eF}{I} = \frac{6 \times 96500}{10}$ = 57900 s = 16h

5 No of mol of $S_2O_3^{2-}$ = 0.0225 x 0.20 = 4.5 x 10^{-3}

No of mol of I_2 evolved = ½ x 4.5 x 10^{-3} = 2.25 x 10^{-3} = no of mol of $S_2O_8^{2-}$

No of mol of electrons = 2 x 2.25 x 10^{-3} = 4.5 x 10^{-3}

using $It = n_eF$

$t = \frac{n_eF}{I} = \frac{4.5 \times 10^{-3} \times 96500}{2}$ = 217 s

6 $Cr^{3+} + 3e \rightarrow Cr$ ——(1)

Let the oxidation of Mn ion be z+

$Mn^{z+} + ze \rightarrow Mn$ —— (2)

No of mol of Mn = $\frac{33}{54.9}$ = 0.601

No of mol of Cr = $\frac{20.8}{52.0} = 0.4$

Mol ratio of Cr : Mn

0.4 : 0.601

4 : 6

Hence eqn (1) x4, eqm (2) x 6, so as to get 4Cr : 6Mn

Equating coefficient of electrons of both half eqns,

6z = 12

z = 2

7 Using the following eqns: F = Le —— (1)

It = n_eF —— (2)

Substitute eqn (1) into (2):

It = n_eLe

Rearranging: L = $\frac{It}{n_e e}$ —— (3)

Cu → Cu^{2+} + 2e

No of mol of Cu oxidised = $\frac{m_1 - m_2}{63.5}$

n_e = 2 x No of mol of Cu oxidised = $\frac{2 \times (m_1 - m_2)}{63.5}$ ——(4)

Sub (4) into (3) : L = $\frac{63.5 \times I \times t}{2 \times e \times (m_1 - m_2)}$

8 using the formula n_eF = It

$n_e = \frac{It}{F}$

since n_e α no of mole of chromium deposited α mass of chromium deposited,

Factors that affect mass of chromium deposited is I – size of current, and t – time duration of electrolysis .

9. A: Cathode is where reduction takes place (recall RED CAT) hence anode is where oxidation takes place. Since reduction is a gain of electrons, and oxidation is a loss of electrons, electrons should be flowing out of the anode and towards the cathode.

B: Electricity is conducted through the flow of electrons through the conducting wire of the external circuit linking the two electrodes.

C: When metallic cations are discharged, they are reduced to their respective metal atoms. More reactive metals have a higher tendency to stay as metal cations and are hence more reluctant to be discharged and reduced to the metal. Hence the ease of discharge of the metal cation is inversely proportional to the reactivity of the metal.

D: $n_{substance} = \frac{It}{zF}$

From the eqn, the amount produced during electrolysis is directly proportional to the amount of electric current, but inversely proportional to the charge on the ions.

10. 1: using the formula $n_{metal} = \frac{It}{zF}$ ——(1)

$$n_{metal} = \frac{Mass_{metal}}{A_r} \text{ —— (2)}$$

Sub eqn (2) into (1): $\frac{It}{zF} = \frac{Mass_{metal}}{A_r}$

Rearranging: $z = \frac{I \times t \times A_r}{F \times Mass_{metal}}$

2: since the solution electrolysed is a nitrate salt, H_2O will be oxidised at the anode to form O_2 gas as nitrate ions, being at the maximum oxidation state, cannot be oxidised at the anode.

3: Mass = $\frac{It}{zF}$ x A_r

From the above eqn, it can be seen that concentration of electrolyte is not a factor that affects the mass of X obtained.

11 1: Since rhodium ions is discharged at the cathode, rhodium ions are cations and positively charged. Cathode is where reduction takes place and only cations and neutral molecules can be reduced.

2: The charge of one mol of electron is given by Faraday's Constant, 9.64 x 10^4 C mol^{-1}. Since the charge of 1 mol of rhodium ion is 3 times the no of Faraday's Constant, $(\frac{2.90 \times 10^5}{9.64 \times 10^4} = 3)$, the magnitude of charge of the rhodium ion is 3 times the charge of an electron.

3: There is insufficient information given in the question to help us conclude that rhodium is a transition element.

Structured

1 a Anode [O]: $2I^- \rightarrow I_2 + 2\,e$

Brown solution of iodine formed.

Cathode [R]: $2\,H_2O + 2\,e \rightarrow H_2 + 2\,OH^-$

Effervescence seen and solution around cathode turns pink due to formation of OH^-.

b $E^\theta_{cell} = -0.54 - 0.83 = -1.37$ V

Minimum voltage = 1.37 V

c

Half–cell	E^e/ V
$Pb \rightleftharpoons Pb^{2+} + 2e$	–0.13
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54

At the anode, Pb is oxidised to Pb^{2+}, while iodide ions are not oxidised as E^e_{ox} of Pb is more positive. Pb^{2+} then combines with I^- to form bright yellow ppt that coats the Pb electrode.

$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

At the cathode: no change in reaction and obersvations.

[R]: $2\,H_2O + 2\,e \rightarrow H_2 + 2\,OH^-$

2 a Cathode [R]: $Sr^{2+}(l) + 2e \rightarrow Sr(l)$

Anode [O]: $2\,Br^-(l) \rightarrow Br_2(l) + 2\,e$

b To prevent the reactive Sr metal from contact with oxygen and water vapour in the air.

c No. of moles of Sr = $\frac{1000}{87.6}$ =11.42 mol

No. of moles of electrons = 11.42 x 2 = 22.83 mol

Q = 22.83 x 96500 = 2.203×10^6 C

Time required = $\frac{2.203 \times 10^6}{25.0}$ = 24.5 h(8.813×10^4 s)

d H_2O has a larger E^θ_{red} than Sr^{2+} , hence H_2O will be preferably reduced.

H_2 gas evolved instead of Sr metal formed.

3 (a) (i) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(ii) Amount of gas collected $= \frac{0.0104}{24} = 4.33 \times 10^{-4}$ mol

Amount of electrons $= 4 \times 4.33 \times 10^{-4} = 1.73 \times 10^{-3}$ mol

Using Q = It = nF,

$I \times (2 \times 60 \times 60) = (1.73 \times 10^{-3})(96500)$

I = 0.0232 A

(C) Electrochemical and Electrolytic Cells

1(a)(i) $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

(ii) positive; $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(iii) $CH_4 \equiv 8e^-$

η_{CH_4} needed per day $= \frac{1}{8}\eta_e$ needed per day $= \frac{1}{8} \times \frac{It}{F} = \frac{1}{8} \times \frac{6 \times 24 \times 60 \times 60}{96500}$ mol

Mass of $CH_4(g) = \frac{1}{8} \times \frac{6 \times 24 \times 60 \times 60}{96500} (12 + 4 \times 1.0) =$ **0.672 g**

(b)

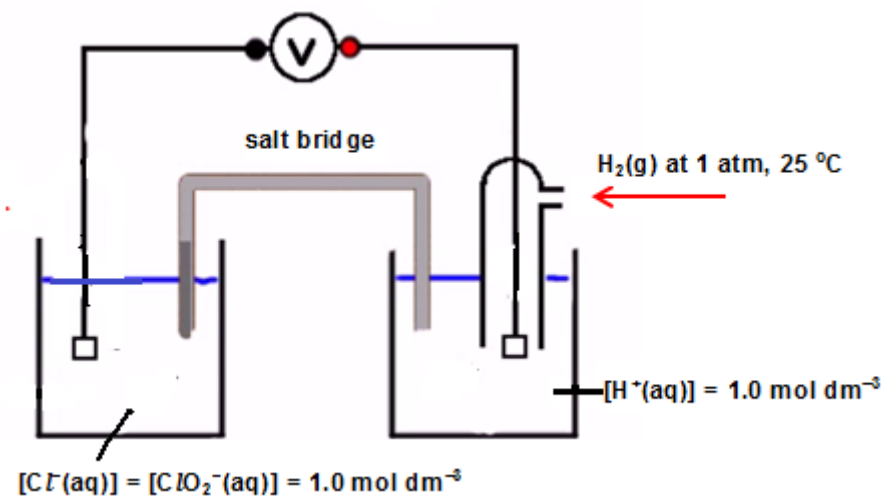
Half–cell	$E^\ominus$/ V
$MnO_2 + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.69

For reduction of MnO_2 to occur, $E^\ominus_{cell} = E^\ominus_{MnO2} - E^\ominus_{M} > 0$ and is only true for Fe^{2+}, where $E^\ominus_{cell} = +0.46$ V

Equation for reaction: $2Fe^{2+}(aq) + MnO_2 + 4H^+ \rightarrow 2Fe^{3+}(aq) + Mn^{2+} + 2H_2O$

(c) At anode: O_2 is evolved; at cathode: Mo(s) is produced.

2(a) 2 half–cells: SHE + half–cell for $ClO_2(aq)/2Cl^-(aq)$



(b)(i) $ClO_2(aq) + H_2O_2(aq) \rightarrow 2Cl^-(aq) + 5O_2(g) + 2H^+(aq)$ $E_{cell} = +0.82$ V

(ii) less positive

(c)(i) $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e$

(ii) 8.35×10^{-6} mol dm^{-3}

(iii) $Cl_2(g)$

3(i) $AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$

$Na_2Mn_5O_{10}(s) + 2AgCl\,(s) \rightarrow 2NaCl(aq) + 5MnO_2(s) + 2Ag(s)$

(ii) no. of moles of Na^+ lost = $\frac{5.0}{23.0}$ = 0.2174 mol

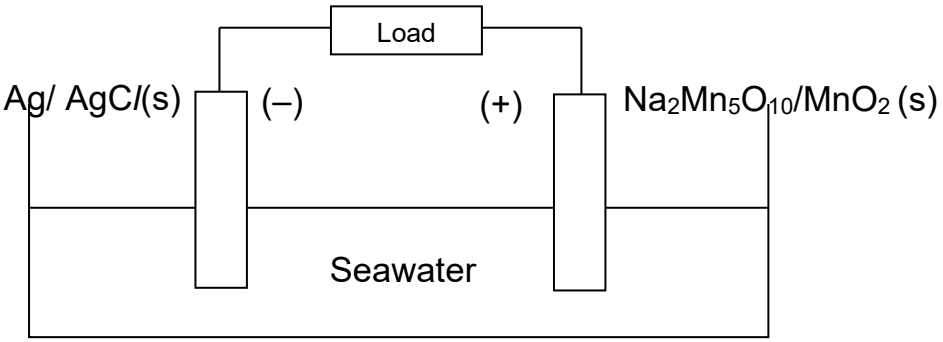
no. of moles of electrons used = 0.2174 mol

Q = 0.2174 x 96500 = 20978 = **2.10×10^4** C

(iii) electrodes: ($Na_2Mn_5O_{10}/MnO_2(s)$ and $Ag/AgCl(s)$;

electrolyte: seawater or 0.600 mol dm^{-3} NaCl

Polarity of electrodes: $Na_2Mn_5O_{10}(s)$ is positive and $Ag/AgCl$ (s) is negative.



(i) At the sodium manganese manganate electrode

$$2Na^+(aq) + 5MnO_2(s) + 2e \rightleftharpoons Na_2Mn_5O_{10}(s)$$

When fresh water is replaced with sea water, $[Na^+]$ increases; by LCP, equilibrium shifts right; electrode potential becomes more positive.

At the silver/silver chloride electrode:

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-(aq)$$

When fresh water is replaced with sea water, $[Cl^-]$ increase; by LCP, equilibrium is shifted to left side.

$\Rightarrow E_{cell}$ becomes less positive.

(v) E_{cell} at end of charing phase = 0.56 – 0.34 = +0.22 V

E_{cell} at start of discharge phase = 0.65 – 0.29 = +0.36 V

Potential gained by system = **+0.14** V

4(a)(i) Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Cathode: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

Overall: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) $E^\ominus_{O2/H2O}$ = +1.23 V

$E^\ominus_{cell} = E^\ominus_{O2/H2O} – E^\ominus_{CO2/C2H5OH}$

$1.61 = 1.23 – E^\ominus_{CO2/C2H5OH}$

$E^\ominus_{O2/C2H5OH} = –0.38$ V

(iii) Ethanol is more energy–efficient than methanol.

Or Ethanol can be obtained in great quantity (or easily obtained) from a fermentation process

(b)(i) From the equations: $CO_2 \equiv 6e^- \equiv 3Cu$

$$\eta_e \text{ passed} = 2 \times \eta_{Cu} \text{ deposited} = 2 \times \frac{31.75}{63.5} = 1.0 \text{ mol}$$

$$\eta_{CO_2} \text{ produced} = \frac{1}{6} \text{ mol}$$

Volume of CO_2 produced = $\frac{1}{6}$ x 24 = **4.00** dm^3

(ii) number of moles of electrons passed $= 1 = \frac{It}{96500}$

$$I = \frac{96500}{8 \times 60 \times 60}$$

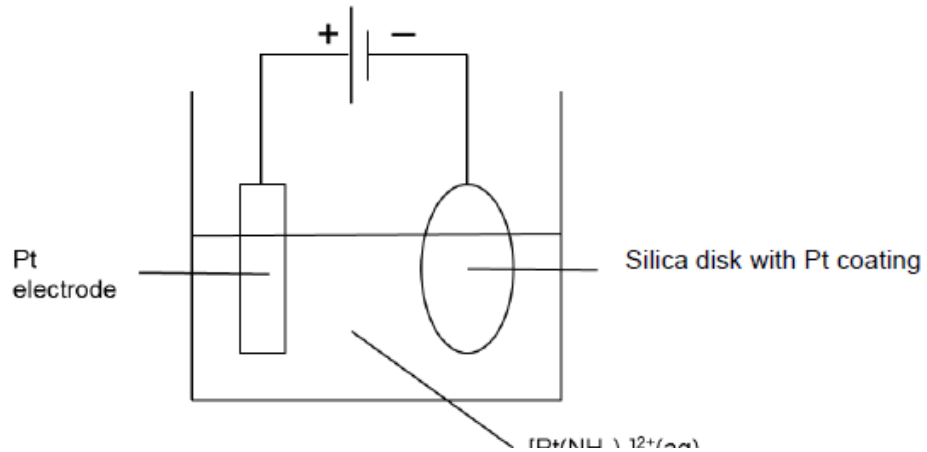
5a(i) (Pt) Cathode (+ve): $O_2 + 4H^+ + 4e \rightarrow 2H_2O$ [1]
(Pd) Anode (-ve): $CH_2CHCH_3 + 2H_2O \rightarrow CH_2CHCOOH + 6H^+ + 6e$ [1]

a(ii) $E_{cell} = E_{[R]} - E_{[O]}$
$E_{[R]} = 0.70 + 0.53 = +1.23$ V [1]

a(iii) $O_2 + 4H^+ + 4e \rightleftharpoons H_2O$
From the Data Booklet, $E°(O_2/H_2O) = +1.23$V at 298K
Since the $E(O_2/H_2O)$ at 298K and at 365K are the same (+1.23V),
$E(O_2/H_2O)$ is independent of temperature. [1]

The operation temperature of the fuel cell need not be increased. [1]

5b(i)



5b(ii) $[Pt(NH_3)_4]^{2+} + 2e \rightarrow Pt + 4NH_3$ [1]
(must be full arrow, redox reaction is irreversible)

5b(iii) $2H_2O + 4e \rightleftharpoons H_2 + 4OH^-$ –0.83 V
$E([Pt(NH_3)_4]^{2+}/Pt)$ has to be more +ve / less –ve than –0.83 V [1]
otherwise H_2O will be prefentially reduced. [1]

5b(iv) Mass of Pt coated = (21.5)(0.40 x 2.00) = 17.2 g
Amount of electrons passed during coating = (17.2 / 195)(2) = 0.1764 mol [1]

$(CH_2CHCH_3 + 2H_2O \rightarrow CH_2CHCOOH + 6H^+ + 6e)$
6 mol of electrons are required per mol of acrylic acid generated.
Amount of acrylic acid = 0.1764 / 6 = 0.02940 mol
Mass of acrylic acid = 0.02940 x 72.0 = 2.12 g [1]