1. (a) When solid calcium nitrate is heated, brown fumes of nitrogen dioxide, NO_2, are seen and the solid remaining after decomposition is calcium oxide.

(i) Write a balanced equation for the thermal decomposition of calcium nitrate.

.....

(2)

(ii) Describe the changes you would see when cold water is added drop by drop to cold calcium oxide and give the chemical equation for the reaction.

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(3)

(iii) State whether barium nitrate will decompose more easily or less easily than calcium nitrate on heating with a Bunsen burner.

.....

(1)

(iv) Account for the trend in the thermal stability of the nitrates of the elements in group 2.

.....

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(3)

(b) The brown fumes in part (a) are not pure NO_2 but a mixture of N_2O_4 and NO_2.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
Pale yellow dark brown

A transparent glass syringe was filled with the gaseous mixture of N_2O_4 and NO_2 and its tip sealed. When the piston of the syringe was rapidly pushed well into the body of the syringe, thereby compressing the gas mixture considerably, the colour of the gas became momentarily darker but them became lighter again.

(i) Suggest why compressing the gases causes the mixture to darken.

.....

.....

(1)

(ii) Explain why the mixture turns lighter on standing.

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.....

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(2)

(iii) Write an expression for the equilibrium constant, K_p, for this equilibrium.

(1)

(iv) 1.0 mole of N_2O_4 was allowed to reach equilibrium at 400K. At equilibrium the partial pressure of N_2O_4 was found to be 0.15 atm.

Given that the equilibrium constant K_p for this reaction is 48 atm, calculate the partial pressure of NO_2 in the equilibrium mixture.

(3)
(Total 16 marks)

2. (a) (i) Calculate the concentration, in mol dm^{-3}, of a solution of hydrochloric acid, HCl, which has a pH of 1.13.

(1)

(ii) Calculate the concentration, in mol dm^{-3} , of a solution of chloric(l) acid, HOCl, which has a pH of 4.23.
Chloric(l) acid is a weak acid with $K_a = 3.72 \times 10^{-8}$ mol dm^{-3}.

(4)

(b) The pH of 0.100 mol dm^{-3} sulphuric acid is 0.98.

(i) Calculate the concentration of hydrogen ions, H^+, in this solution.

(1)

(ii) Write equations to show the two successive ionisations of sulphuric acid, H_2SO_4, in water.

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.....

(2)

(iii) Suggest why the concentration of hydrogen ions is not 0.20 mol dm^{-3} in 0.100 mol dm^{-3} sulphuric acid.

.....

.....

(1)

(c) Many industrial organic reactions produce hydrogen chloride as an additional product. This can be oxidised to chlorine by the Deacon process:

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g) \quad \Delta H = -115 \text{ kJ mol}^{-1}.$$

0.800 mol of hydrogen chloride was mixed with 0.200 mol of oxygen in a vessel of volume 10.0 dm^3 in the presence of a copper(I) chloride catalyst at 400 ºC. At equilibrium it was found that the mixture contained 0.200 mol of hydrogen chloride.

(i) Write an expression for the equilibrium constant K_c.

(1)

(ii) Calculate the value of K_c at 400 ºC.

(4)

(d) State and explain the effect, if any, on the **position of equilibrium** in (c) of:

(i) decreasing the temperature;

.....

.....

.....

(2)

(ii) decreasing the volume;

.....

.....

.....

(2)

(iii) removing the catalyst.

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.....

(2)

(Total 20 marks)

3. The reaction between sulphur dioxide and oxygen is a dynamic equilibrium.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -196 \text{ kJmol}^{-1}$$

(a) Explain what is meant by **dynamic equilibrium**.

.....

.....

.....

(2)

(b) In the table below state the effect on this reaction of increasing the temperature and of increasing the pressure.

	Effect on the rate of the reaction	Effect on the position of equilibrium
Increasing the temperature	Increases	
Increasing the pressure		

(3)

(c) This reaction is one of the steps in the industrial production of sulphuric acid. The normal operating conditions are a temperature of 450 °C, a pressure of 2 atmospheres and the use of a catalyst.

Justify the use of these conditions.

(i) A temperature of 450 °C:

.....

.....

.....

(3)

(ii) A pressure of 2 atmospheres:

.....

.....

.....

(2)

(iii) A catalyst:

.....

.....

.....

(1)

(d) Give the name of the catalyst used.

.....

(1)

(e) Give one large scale use of sulphuric acid.

.....

(1)

(Total 13 marks)

4. (a) What is meant by the term **weak acid**?

.....

.....

.....

(2)

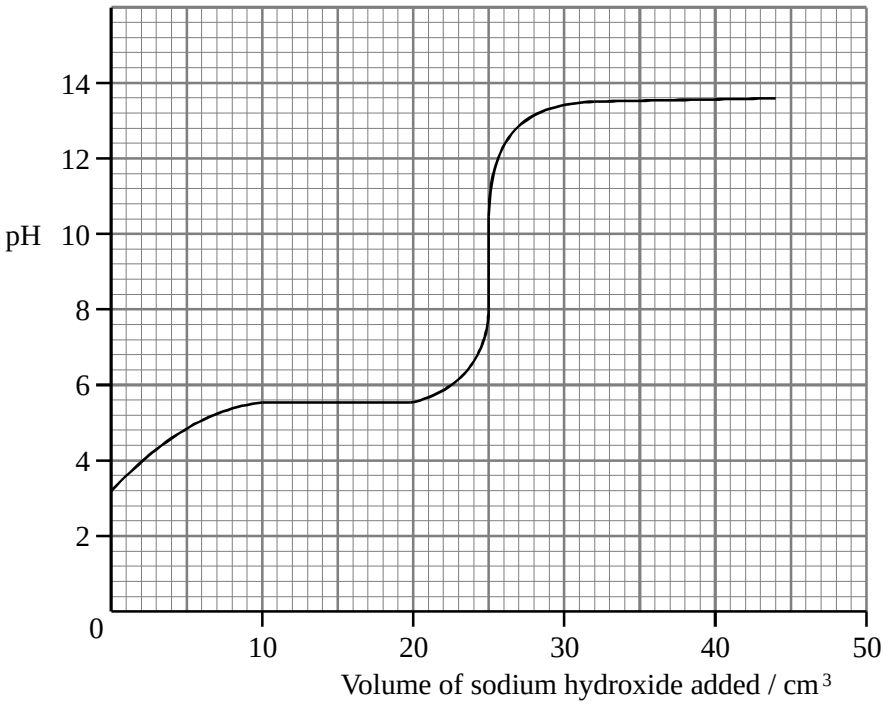
(b) A weak acid, represented by HA, dissociates in water according to the equation:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

Write an expression for the dissociation constant, K_a, for HA.

(1)

(c) 25 cm^3 of 1.00 mol dm^{-3} aqueous HA, was titrated with 1.00 mol dm^{-3} aqueous sodium hydroxide and the pH measured throughout. The titration curve is shown below.



Use the titration curve to find:

(i) the value of the pH at the end point of the titration.

.....

(1)

(ii) the pH of an aqueous solution of the salt NaA.

.....

(1)

(iii) the value of pK_a for the acid HA and, hence the value K_a.

pK_a .....

K_a .....

(2)

(d) Some of the solutions made during this titration would act as buffer solutions.

(i) What is meant by the term **buffer solution**?

.....

.....

.....

(2)

(ii) Use the titration curve to find:

the range of pH values over which this mixture acts as a buffer;

from ..... to .....

(1)

the pH of the most efficient buffer solution.

.....

(1)

(e) Suggest, with reasoning, whether methyl orange or phenolphthalein would be the better indicator for this titration.

Choice .....

Reasoning .....

.....

.....

(3)

(f) Explain why, as the titration proceeds, the flask becomes warm but not as warm as it would in a similar titration using 1.00 mol dm^{-3} solutions of hydrochloric acid and sodium hydroxide.

.....

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(3)

(g) A different monobasic weak acid has a dissociation constant of 1.8×10^{-5} mol dm^{-3}.

(i) Define pH.

.....

(1)

(ii) Calculate the pH of a 1.00 mol dm^{-3} aqueous solution of this acid.

(3)
(Total 21 marks)

5. In the vapour phase sulphur trioxide dissociates:

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

(a) (i) Write an expression for K_p for this dissociation.

(1)

(ii) At a particular temperature, 75% of the sulphur trioxide is dissociated, producing a pressure of 10 atm. Calculate the value of K_p at this temperature paying, attention to its units.

(5)

(b) Solid vanadium(V) oxide, V_2O_5, is an effective catalyst for this reaction. State the effect of using double the mass of catalyst on:

(i) the position of the equilibrium;

.....

.....

(1)

(ii) the value of K_p.

.....

.....

(1)

(Total 8 marks)

6. (a) Methane reacts with steam in a reversible reaction. In industry this reaction, carried out at a pressure of 30 atm, is used to produce hydrogen for the manufacture of ammonia

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +210 \text{ kJ mol}^{-1}$$

(i) Define the term **partial pressure** as applied to a gas mixture.

.....

.....

(1)

(ii) Write an expression for the equilibrium constant, K_p, for this reaction.

(1)

(iii) State and explain the effect of increasing the total pressure on the position of this equilibrium;

.....

.....

.....

.....

.....

(2)

(b) State the effect on the value of K_p for this equilibrium of the following.

(i) Increasing the total pressure.

.....

(1)

(ii) Increasing the temperature.

.....

(1)

(iii) Adding a catalyst.

.....

(1)

(c) There is a theory that methane, CH_4, constantly leaks from the earth's crust. This is not noticeable on land but at the bottom of a cold sea, such as off the Canadian coast, the methane is trapped in a solid cage of water molecules.

$$CH_4(g) + 6H_2O(s) \rightleftharpoons [CH_4(H_2O)_6](s)$$

methane hydrate

At –29 °C the equilibrium pressure of the methane is 101.3 kPa.

(i) Write an expression for K_p for this equilibrium.

(1)

(ii) Deduce the value of K_p at –29 °C, stating its units.

(1)

(iii) At 0 °C the equilibrium pressure of methane rises to 2600 kPa. What does this tell you about the effect of temperature change on the position of equilibrium and about the enthalpy change for this reaction?

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(2)

(iv) Some people have suggested collecting the methane hydrate from the bottom of the sea and allowing it to warm up to 0 °C on board a ship. Comment on whether this would be a useful method for collecting methane.

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(1)
(Total 12 marks)

7. Ethanoic acid, CH_3COOH, is a weak acid which can be used, with its salts, to make buffer solutions.

(a) Explain what is meant by the term **weak acid**.

.....

.....

(1)

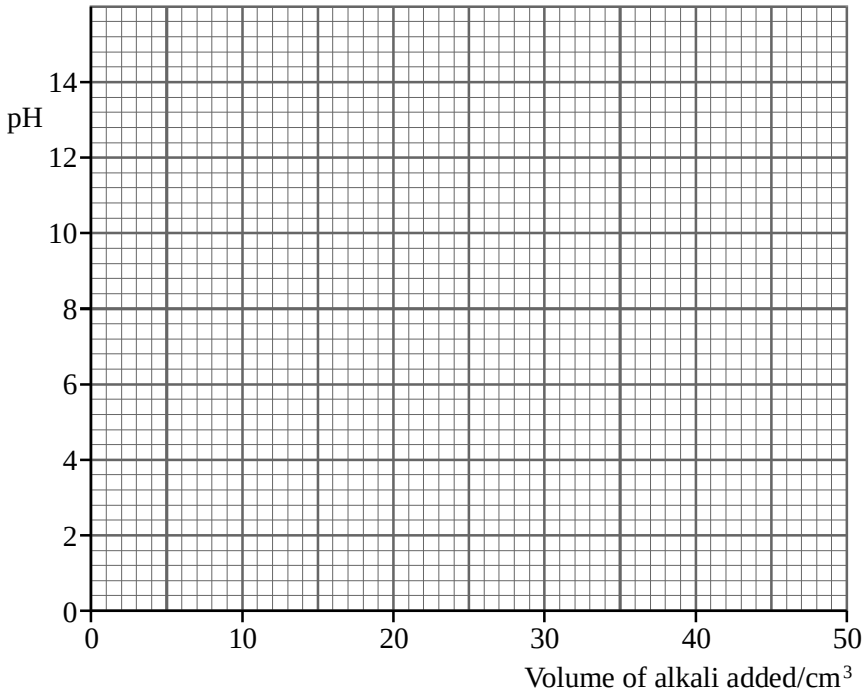
(b) Explain what is meant by the term **buffer solution**.

.....

.....

(2)

(c) An aqueous solution of ethanoic acid of concentration 1.00 mol dm^{-3} has a pH of 2.8. Sketch, with care, how the pH changes during the titration of 25.0 cm^3 1.00 mol dm^{-3} aqueous ethanoic acid with aqueous sodium hydroxide of the same concentration.



(4)

(d) Indicate on your sketch the portion of the curve where the mixture is behaving as a buffer.

(1)

(e) (i) Write an expression for the dissociation constant, K_a, for ethanoic acid.

(1)

(ii) Explain how the p*K*a of ethanoic could be found from the graph.

.....

.....

(2)

(Total 11 marks)

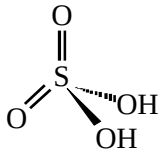
8. (a) The first stage in the manufacture of sulphuric acid is the Contact Process.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

At 400 °C the equilibrium constant $K_p = 3.00 \times 10^4$ atm^{-1}. A catalyst of vanadium(V) oxide is used. In a particular equilibrium mixture at 400 °C the partial pressures of sulphur dioxide and of oxygen were 0.100 atm and 0.500 atm respectively. Show that the yield of SO_3 is about 95% of the equilibrium mixture.

(5)

(b) (i) Pure sulphuric acid is a viscous liquid with a high boiling temperature of 338 °C. It has the structure:



Suggest in terms of the intermolecular forces in sulphuric acid why it has such a high boiling temperature.

(3)

(ii) Sulphuric acid dissolves in water in a highly exothermic reaction

May her rest be long and placid,
She added water to the acid;
The other girl did what we taught her,
And added acid to the water.

Suggest why sulphuric acid must always be added to water to dilute it rather than the other way round.

(2)

(c) Sulphuric acid dissociates in water according to the equations:

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

The dissociation constant for the first dissociation is very large; that for the second is 0.01 mol dm^{-3} at 25 °C.

(i) Calculate the pH of an aqueous solution containing 0.200 mol dm^{-3} hydrogen ions.

(1)

(ii) The pH of 0.100 mol dm^{-3} sulphuric acid is 0.98. Explain why this is so close to the pH of 0.100 mol dm^{-3} HCl which is 1.0.

(3)

(d) Sulphuric acid is used as the electrolyte in the lead-acid battery found in cars. The electrodes are made from lead and from lead(IV) oxide. As the cell discharges, the lead and the lead(IV) oxide are both converted to lead(II) sulphate, and the sulphuric acid concentration falls.

(i) Use the information above to deduce the two half equations occurring in the lead acid battery.

(3)

(ii) Hence write an equation to represent the overall process taking place as the cell discharges.

(1)

(Total 18 marks)

9. (a) Define the following terms.

(i) pH .....

(1)

(ii) K_w .....

(1)

(b) Explain the meaning of the term **strong**, as applied to an acid or a base.

……...…….……..

……...…….……..

(1)

(c) Calculate the pH of the following solutions.

(i) HCl(aq) of concentration 0.200 mol dm^{-3}.

(1)

(ii) NaOH (aq) of concentration 0.800 mol dm^{-3} ($K_w = -1.00 \times 10^{-14}$ mol^2 dm^{-6}).

(2)

(d) HA is a weak acid with a dissociation constant $K_a = 5.62 \times 10^{-5}$ mol dm^{-3}.

(i) Write an expression for the dissociation constant, K_a, of HA.

(1)

(ii) Calculate the pH of a 0.400 mol dm^{-3} solution of HA.

(3)

(e) A buffer solution contains HA(aq) at a concentration of 0.300 mol dm^{-3}, and its sodium salt, NaA, at a concentration of 0.600 mol dm^{-3}. Calculate the pH of this buffer solution.

(3)
(Total 13 marks)

10. Consider the following equation:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

2.0 moles of SO_2 and 1.0 mole of O_2 were allowed to react in a vessel of volume 60 dm^3.
At equilibrium 1.8 moles of SO_3 had formed and the pressure in the flask was 2 atm.

(a) (i) Write the expression for K_c for this reaction between SO_2 and O_2.

(1)

(ii) Calculate the value of K_c, with units.

(3)

(b) The reaction between SO_2 and O_2 is exothermic. State the effect on the following, if the experiment is repeated at a higher temperature:

(i) K_c ……..

(1)

(ii) the equilibrium position .....

(1)

(c) State the effect of a catalyst on:

(i) K_c ……..

(1)

(ii) the equilibrium position .....

(1)

(d) (i) Write the expression for K_p for the reaction between SO_2 and O_2.

(1)

(ii) Calculate the mole fractions of SO_2, O_2 and SO_3 at equilibrium.

(2)

(iii) Calculate the partial pressures of SO_2, O_2 and SO_3 at equilibrium.

(1)

(iv) Calculate the value of K_p, with units.

(2)
(Total 14 marks)

11. Thermochemical data, at 298 K, for the equilibrium between zinc carbonate, zinc oxide and carbon dioxide is shown below.

$$ZnCO_3(s) \rightleftharpoons ZnO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +71.0 \text{ kJ mol}^{-1}$$

$$S^{\ominus}[ZnO(s)] = +43.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^{\ominus}[ZnCO_3(s)] = +82.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^{\ominus}[CO_2(g)] = +213.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

(a) (i) Suggest reasons for the differences between the three standard entropies.

.....

.....

.....

.....

(2)

(ii) Calculate the entropy change for the system, $\Delta S^{\ominus}_{\text{system}}$, for this reaction. Include the sign and units in your answer.

(2)

(b) Calculate the entropy change for the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K, showing your method clearly.

(2)

(c) (i) Calculate the total entropy change for this reaction, $\Delta S^{\ominus}_{total}$, at 298 K.

(1)

(ii) What does the result of your calculation in (c)(i) indicate about the natural direction of this reaction at 298 K?

Justify your answer.

.....

.....

(1)

(d) (i) Write an expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) State how you would alter ONE condition to increase the yield of carbon dioxide from this equilibrium reaction.

Justify your answer.

.....

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.....

(2)

(Total 11 marks)

12. Propanoic acid is a weak acid which dissociates according to

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

(a) (i) Indicate, in the space provided below the equation, the two acid/base conjugate pairs.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, for propanoic acid.

(1)

(iii) Calculate the pH of a 0.100 mol dm^{-3} solution of propanoic acid, for which $K_a = 1.3 \times 10^{-5}$ mol dm^{-3}.

(3)

(iv) Calculate the concentration of hydroxide ions, OH^-, in this same solution of propanoic acid. $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at the temperature of the solution.

(3)

(b) If sodium propanoate is dissolved in water, the pH of the resulting solution is not 7, but is near to 8. By writing the equation for the reaction occurring suggest why this is so.

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.....

.....

(2)

(c) A mixture of sodium propanoate and propanoic acid behaves as a buffer solution.

(i) What is meant by a **buffer solution**?

.....

.....

.....

(2)

(ii) Calculate the pH of a buffer solution that is made by mixing equal volumes of 0.0500 mol dm^{-3} propanoic acid and 0.100 mol dm^{-3} sodium propanoate.

(3)
(Total 16 marks)

13. A saturated solution of calcium hydroxide, $Ca(OH)_2(aq)$, has a pH of 9.6.

(a) Write an expression linking hydrogen ion concentration and pH. Use this to calculate the concentration of hydrogen ions in this solution.

(3)

(b) (i) The ionisation constant for water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}.

Write the expression for K_w.

$K_w =$

(1)

(ii) Calculate the concentration of hydroxide ions in the saturated solution of calcium hydroxide.

(1)

(iii) Calculate the concentration of calcium hydroxide in the saturated solution.

(1)

(iv) Calculate the solubility of calcium hydroxide in g dm^{-3}.

Give your answer to three significant figures.

(1)

(v) Suggest why your calculated value may differ significantly from the value in chemistry reference books.

.....

.....

(1)

(c) An alternative method for finding the solubility of calcium hydroxide is to titrate 100 cm^3 of the saturated solution with hydrochloric acid of concentration 0.00100 mol dm^{-3}.

$$Ca(OH)_2\ (aq) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + 2H_2O\ (l)$$

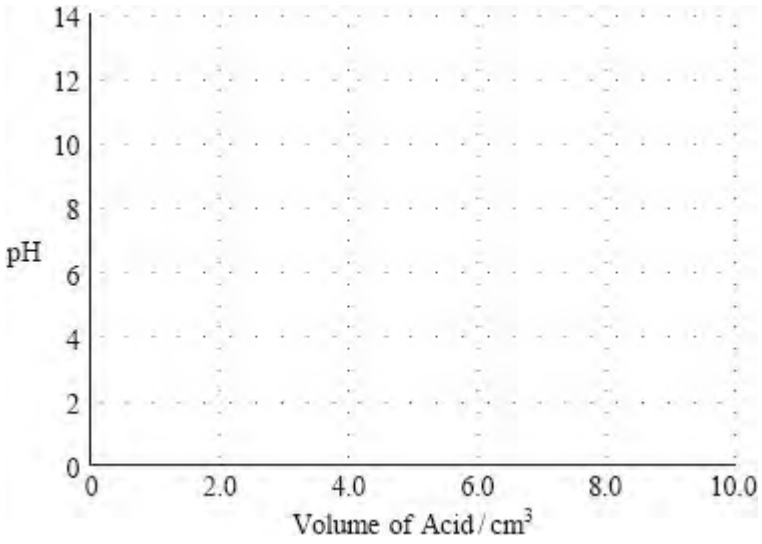
(i) Calculate the pH of the hydrochloric acid.

(1)

(ii) Use your answer to (b)(iii) and the information above to calculate the volume of hydrochloric acid needed to neutralise 100 cm^3 of the saturated calcium hydroxide solution.

(3)

(iii) Sketch the titration curve for this reaction.



(2)

(iv) Suggest why phenolphthalein is **not** a suitable indicator for this reaction.

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(1)

(Total 15 marks)

14. (a) Ammonia reacts with water as below:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

A 0.100 mol dm^{-3} solution of ammonia has a pH of 11.13.

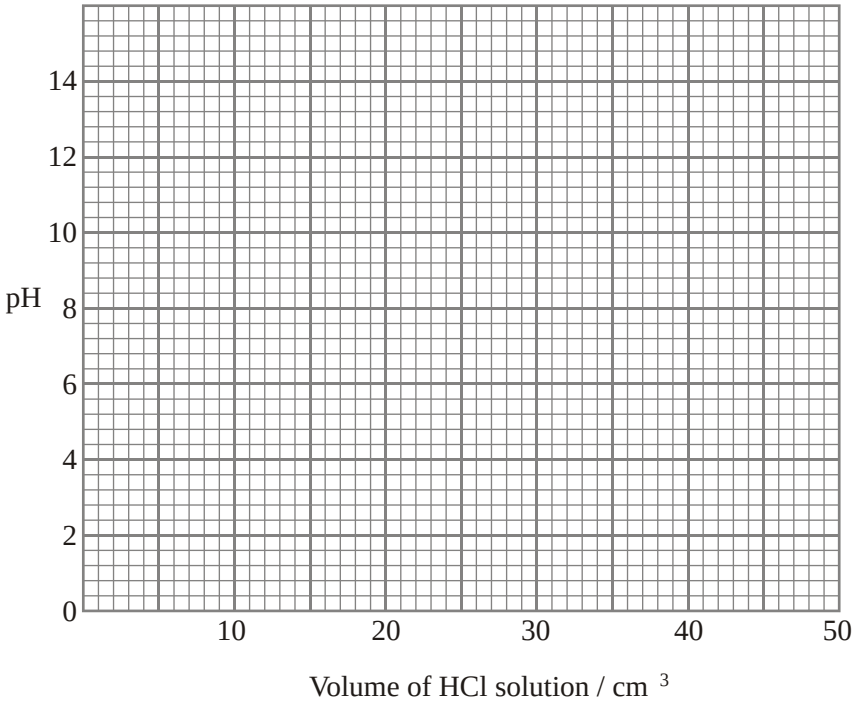
(i) Identify the Bronsted–Lowry acid/base conjugate pairs in the equation. Clearly label which are acids and which are bases.

.....

.....

(2)

(ii) Draw, on the axes below, a graph to show how the pH of the solution varies as 40 cm^3 of 0.100 mol dm^{-3} hydrochloric acid (a strong acid) is added slowly to 20 cm^3 of the ammonia solution.



(4)

(iii) Select, from the following list, the indicator which would be the most suitable for this titration. Give a reason for your choice.

Indicator	pK_{ind}	Range
methyl red	5.1	4.2–6.3
bromothymol blue	7.0	6.0–7.6
phenolphthalein	9.3	8.2–10.0

Indicator: .....

Reason: .....

.....

(2)

(b) Nitrous acid, HNO_2, is a weak acid with an acid dissociation constant $K_a = 4.70 \times 10^{-4}$ mol dm^{-3} at 4 °C.

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

(i) Write the expression for K_a.

(1)

(ii) Calculate the pH of a 0.120 mol dm^{-3} solution of nitrous acid.

(3)

(iii) Calculate the pH of a buffer solution made by adding 1.38 g of sodium nitrite, $NaNO_2$, to 100 cm^3 of the 0.120 mol dm^{-3} solution of nitrous acid ($K_a = 4.70 \times 10^{-4}$ mol dm^{-3}).

(4)

(iv) Suggest why a mixture of nitrous acid and sodium nitrite can act as a buffer solution whereas a solution of sodium nitrite on its own does not.

.....

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.....

.....

(2)

(Total 18 marks)

15. When dinitrogen tetroxide, N_2O_4, dissociates, the following equilibrium is established.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(a) State a property which could be measured to follow the progress of this reversible reaction.

.....

(1)

(b) Write an expression for the equilibrium constant, K_c, for this reaction.

(1)

(c) When a sample of 0.0370 moles of gaseous dinitrogen tetroxide is allowed to dissociate at 25 °C in a container of volume 1 dm^3, 0.0310 moles of $N_2O_4(g)$ remain in the equilibrium mixture.

Complete the table below, and use the data to calculate K_c for the reaction. Include a unit in your answer.

	N_2O_4	NO_2
Number of moles at start	0.0370	0
Number of moles in 1 dm^3 at equilibrium	0.0310	

K_c calculation:

(3)

(d) The reaction was repeated at a higher pressure, maintaining the temperature at 25 °C.

(i) How does this increase in pressure affect the amount of nitrogen dioxide, $NO_2(g)$, in the equilibrium mixture?

.....

(1)

(ii) How does this increase in pressure affect the value of K_c?

.....

(1)

(e) The reaction was repeated at the original pressure, but the temperature was increased to 75 °C. The value of K_c was approximately twenty times greater.

How does this information show that the reaction is endothermic?

.....

.....

.....

(1)

(f) Predict the sign of ΔS_{system} for the reaction, giving a reason for your answer.

.....

.....

.....

(2)

(g) Write the equation for the relationship between $\Delta S_{surroundings}$ and ΔH for the reaction.

(1)

(h) The magnitude of ΔS_{system} for the reaction is greater than the magnitude of $\Delta S_{surroundings}$. Explain why this must be the case.

.....

.....

.....

.....

(2)

(Total 13 marks)

16. (a) (i) Use an equation to define the term pH.

.....

(1)

(ii) Explain how some solutions can have a negative pH.

.....

.....

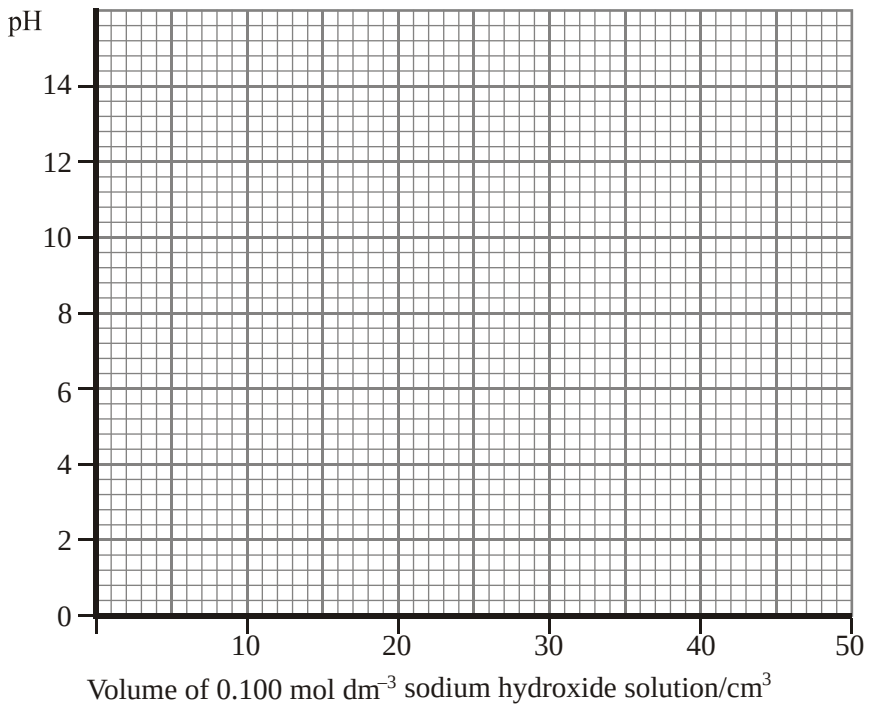
(1)

(b) The concentration of propanoic acid can be found by titrating a sample with standard sodium hydroxide solution.

(i) Calculate the pH of 0.100 mol dm^{-3} propanoic acid at 25 °C; the value of the dissociation constant for the acid, K_a, is 1.30×10^{-5} mol dm^{-3}.

(3)

(ii) Sketch with reasonable accuracy the titration curve that you would expect if 25.0 cm^3 of 0.100 mol dm^{-3} propanoic acid were to be titrated with 0.100 mol dm^{-3} sodium hydroxide solution.



(iii) What is the significance of the pH of the mixture when 12.5 cm^3 of sodium hydroxide had been added to the propanoic acid?

.....

(1)

(Total 10 marks)

17. This question concerns the equilibrium

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad \Delta H = -180 \text{ kJ mol}^{-1}$$

(a) Define the term **partial pressure**.

.....

.....

(1)

(b) (i) Write the expression for K_p for the above reaction.

(1)

(ii) At 1600 °C and 1.5 atm pressure NO is 99 % dissociated at equilibrium. Calculate the value of K_p under these conditions.

(4)

(c) State and explain the effect on K_p and hence on the position of equilibrium of decreasing the temperature at constant pressure.

.....

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.....

.....

(3)

(d) The reaction

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

is used to purify nickel.

(i) Write the expression for K_p for this system.

(1)

(ii) In order to achieve a high equilibrium yield of $Ni(CO)_4$ should a low or a high partial pressure of carbon monoxide be used? Explain your answer in terms of K_p.

.....

.....

.....

(2)
(Total 12 marks)

18. The equation below shows a possible reaction for producing methanol.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l) \qquad \Delta H^{\ominus} = -129 \text{ kJ mol}^{-1}$$

(a) The entropy of one mole of each substance in the equation, measured at 298 K, is shown below.

Substance	$S^{\ominus}$ /J mol^{-1} K^{-1}
CO(g)	197.6
H_2(g)	130.6
CH_3OH(l)	239.7

(i) Suggest why methanol has the highest entropy value of the three substances.

.....

.....

(1)

(ii) Calculate the entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction.

(2)

(iii) Is the sign of $\Delta S^{\ominus}_{system}$ as expected? Give a reason for your answer.

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(1)

(iv) Calculate the entropy change of the surroundings $\Delta S^{\ominus}_{surroundings}$, at 298 K.

(2)

(v) Show, by calculation, whether it is possible for this reaction to occur spontaneously at 298 K.

(2)

(b) When methanol is produced in industry, this reaction is carried out at 400 ºC and 200 atmospheres pressure, in the presence of a catalyst of chromium oxide mixed with zinc oxide. Under these conditions methanol vapour forms and the reaction reaches equilibrium. Assume that the reaction is still exothermic under these conditions.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

(i) Suggest reasons for the choice of temperature and pressure.

Temperature .....

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.....

.....

Pressure .....

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(3)

(ii) The catalyst used in this reaction is **heterogeneous**. Explain this term.

.....

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(1)

(iii) Write an expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

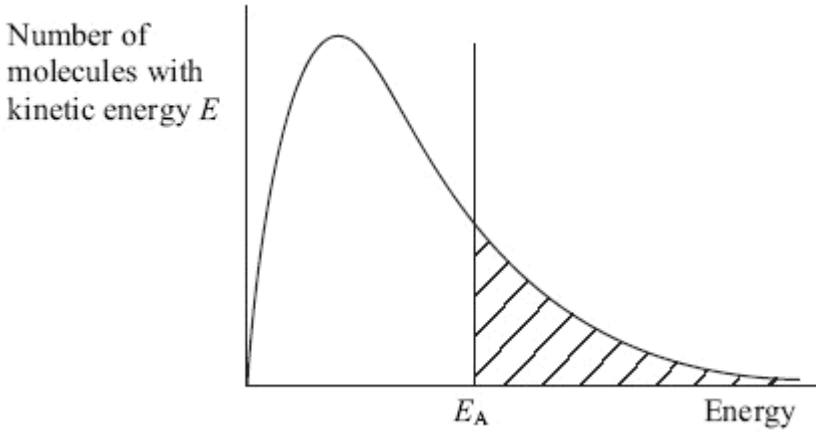
(1)

(iv) In the equilibrium mixture at 200 atmospheres pressure, the partial pressure of carbon monoxide is 55 atmospheres and the partial pressure of hydrogen is 20 atmospheres.

Calculate the partial pressure of methanol in the mixture and hence the value of the equilibrium constant, K_p. Include a unit in your answer.

(2)

(c) The diagram below shows the distribution of energy in a sample of gas molecules in a reaction when no catalyst is present. The activation energy for the reaction is E_A.



(i) What does the shaded area on the graph represent?

.....

(1)

(ii) Draw a line on the graph, labelled $\boldsymbol{E}_C$, to show the activation energy of the catalysed reaction.

(1)

(Total 17 marks)

19. Pentanoic acid, C_4H_9COOH, is a weak acid with an acid dissociation constant, $K_a = 1.5 \times 10^{-5}$ mol dm^{-3}.

(i) What is meant by the term **weak** in a weak acid?

.....

.....

(1)

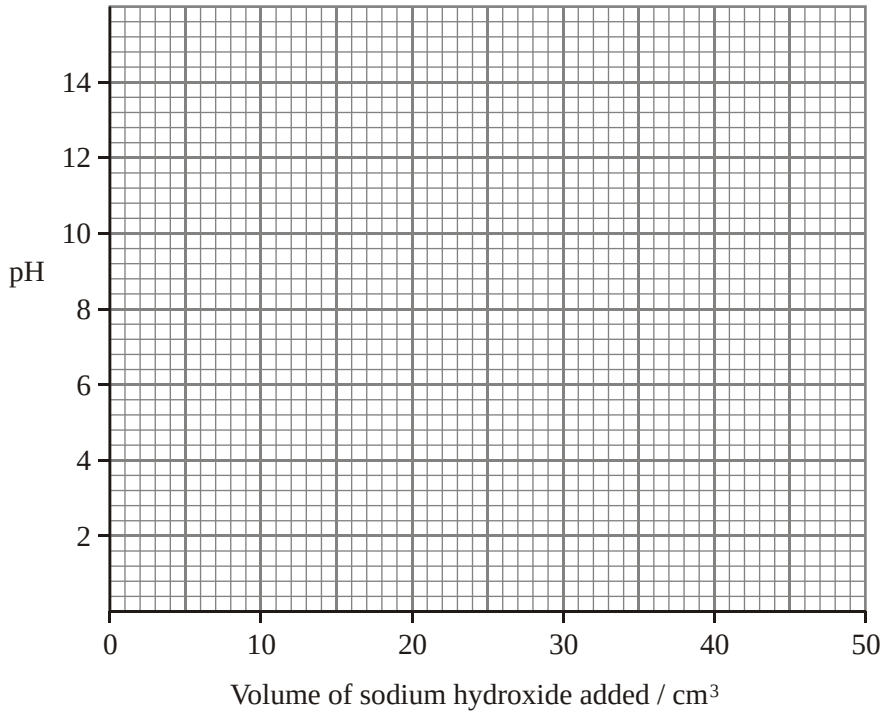
(ii) Write the expression for the K_a of C_4H_9COOH.

(1)

(iii) Calculate the pH of a 0.100 mol dm^{-3} solution of C_4H_9COOH.

(3)

(iv) On the grid below sketch the change in pH during the addition of 50.0 cm^3 of 0.100 mol dm^{-3} sodium hydroxide solution to 25 cm^3 of 0.100 mol dm^{-3} pentanoic acid solution.



(4)

(v) Suggest, with reasoning, a suitable indicator for the titration in (iv).

Indicator	pK_{ind}
Bromophenol blue	4.0
Methyl red	5.1
Thymol blue	8.9
Alizarin yellow	12.5

Indicator .....

Reason .....

.....

(2)

(Total 11 marks)

20. The reaction between nitrogen and hydrogen can be used to produce ammonia.

$$N_2(g) + 3H^2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92.2 \text{ kJ mol}^{-1}$$

Standard entropies are given below

$S^{\ominus}\ [N_2(g)] = +191.6 \text{ J mol}^{-1} \text{ K}^{-1}$

$S^{\ominus}\ [H_2(g)] = +130.6 \text{ J mol}^{-1} \text{ K}^{-1}$

$S^{\ominus}\ [NH_3(g)] = +192.3 \text{ J mol}^{-1} \text{ K}^{-1}$

(a) Calculate the entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$, for this reaction. Include a sign and units in your answer.

(2)

(b) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K. Include a sign and units in your answer.

(2)

(c) (i) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, at 298 K. Include a sign and units in your answer.

(1)

(ii) Is this reaction feasible at 298 K? Justify your answer.

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(1)

(d) In industry the reaction is carried out at about 700 K using an iron catalyst and high pressures.

(i) The yield of ammonia produced at equilibrium is less at 700 K than at 298 K, if the pressure remains constant. In terms of entropy, explain why this happens.

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(1)

(ii) Higher pressures increase the yield of ammonia at equilibrium. Suggest a reason why pressures greater than 300 atmospheres are **not** routinely used.

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(1)

(iii) Iron is a heterogeneous catalyst. Explain what is meant by **heterogeneous**.

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(1)

(Total 9 marks)

21. (a) When silver carbonate is heated, it decomposes into silver oxide and carbon dioxide.

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

At 227 °C, the value of the equilibrium constant, K_p, is 1.48 atm.

(i) Write the expression for the equilibrium constant, K_p.

(1)

(ii) What is the pressure of carbon dioxide gas when silver carbonate is heated to a temperature of 227 °C in a closed vessel?

(1)

(b) When nitrosyl chloride, NOCl, is heated, it dissociates reversibly into nitric oxide, NO, and chlorine, Cl_2, according to the equation

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g) \qquad \Delta H = +75.6 \text{ kJ mol}^{-1}$$

(i) Write the expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) 1.00 mol of nitrosyl chloride was placed in a sealed container and heated to 500 °C. Equilibrium was reached when 22.0% of the nitrosyl chloride had dissociated. The pressure in the vessel was 5.00 atm.

Calculate the value of K_p at this temperature, stating its units.

(5)

(iii) State the effect of an increase in temperature on the value of the equilibrium constant, K_p. Justify your answer.

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(2)

(iv) Hence suggest in which direction the position of equilibrium moves when the temperature is increased. Justify your answer.

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(2)

(Total 12 marks)

22. (a) The first step in the esterification of ethanoic acid, CH_3COOH, by ethanol in the presence of a small quantity of concentrated sulphuric acid, is the reaction

$$CH_3COOH + H_2SO_4 \rightarrow CH_3COOH_2^+ + HSO_4^-$$

In the space below the equation, identify the two acid base conjugate pairs.

(2)

(b) Ethanoic acid, CH_3COOH, is a weak acid and dissociates in water according to the equation

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Its acid dissociation constant, K_a, is

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.74 \times 10^{-5} \text{ mol dm}^{-3} \text{ (at 25 °C)}$$

(i) The concentration of a solution of ethanoic acid can be determined by titrating a 25.0 cm^3 sample in a conical flask against a standard solution of sodium hydroxide.

State whether the pH at the end point is less than 7, 7, or more than 7, and hence name a suitable indicator for this titration.

pH at end point .....

Indicator .....

(2)

(ii) Ethanoic acid is only about 1% ionised in dilute solutions. Its enthalpy of neutralisation is –55 kJ mol^{-1}, whereas the enthalpy of neutralisation of a strong acid, such as hydrochloric acid, is –57 kJ mol^{-1}.

Explain why there is so little difference between these two values.

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(3)

(iii) Calculate the pH of a 0.140 mol dm^{-3} solution of ethanoic acid, clearly showing the TWO assumptions that you have made.

Calculation

Assumptions

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(4)

(iv) To 50.0 cm^3 of the solution in (III) , an equal volume of a 0.200 mol dm^{-3} solution of potassium ethanoate was added. Calculate the pH of the buffer solution obtained.

(3)
(Total 14 marks)

23. In the first stage of an industrial process for purifying nickel, carbon monoxide is passed over impure nickel at 323 K. Gaseous nickel tetracarbonyl, $Ni(CO)_4$, is formed.

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g) \qquad \Delta H^{\ominus} = -191 \text{ kJ mol}^{-1}$$

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction given the following standard entropy values.

Substance	$S^{\ominus}$ /J mol^{-1} K^{-1}
Ni(s)	+29.9
CO(g)	+197.6
$Ni(CO)_4(g)$	+313.4

Include a sign and units in your answer.

(2)

(ii) Refer to the equation above and comment on the sign of your answer.

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(1)

(iii) Calculate $\Delta S^{\ominus}_{\text{surroundings}}$ at 323 K. Include a sign and units in your answer.

(2)

(iv) Deduce the direction of this reaction at 323 K. Justify your answer.

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(1)

(b) (i) Write the expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) 100 moles of gaseous carbon monoxide is mixed with excess solid nickel at 323 K in a vessel kept at 1.00 atmosphere pressure. At equilibrium, 1.00 mole of the carbon monoxide has reacted.

Complete the table below and then calculate the value of K_p at this temperature. Include the units of K_p in your answer.

Substance	Moles at start	Moles at equilibrium	Partial pressure, p_{eq} /atm
$Ni(CO)_4$	0		
CO	100	99.0	

(4)

(iii) As K_p has such a small value, suggest THREE ways in which this industrial process could be improved to increase profitability. Justify each of your suggestions.

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(3)

(c) The second stage of this process is to recover the nickel from the nickel tetracarbonyl, $Ni(CO)_4$. By considering your calculations of the entropy changes, suggest how this could be done. Justify your suggestion.

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(2)
(Total 16 marks)

24. The weak acid methanoic acid, HCOOH, sets up the following equilibrium in water at 298 K:

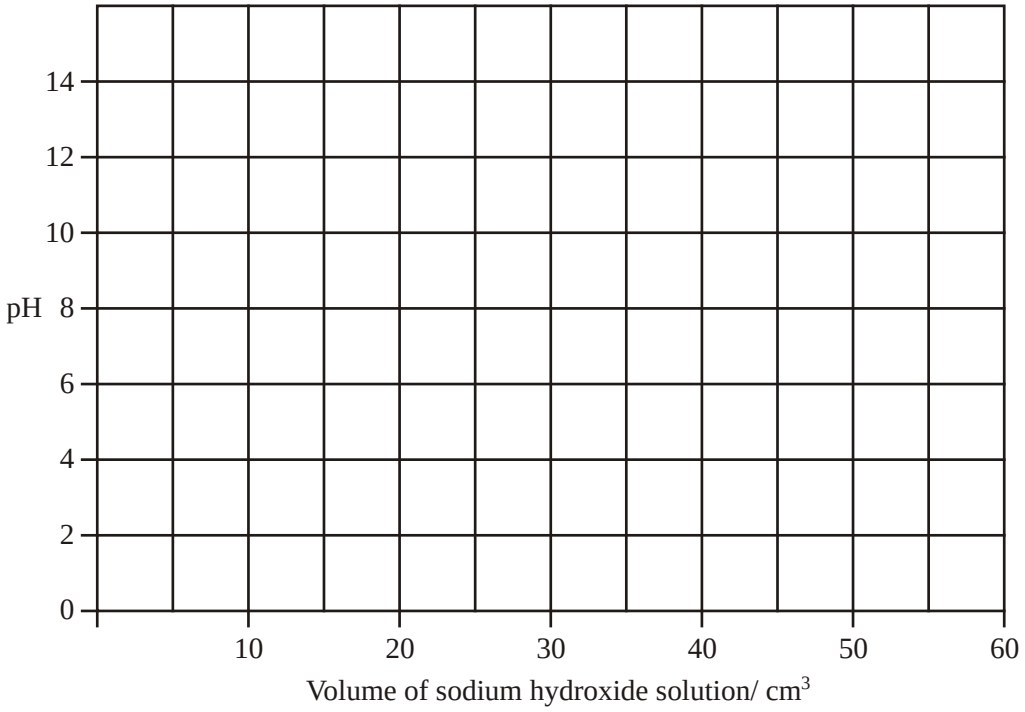
$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

The acid dissociation constant, K_a, for methanoic acid at 298 K is 1.78×10^{-4} mol dm^{-3}.

(a) A 0.200 mol dm^{-3} solution of methanoic acid has a pH of 2.2 at 298 K.

20.0 cm^3 of this solution is titrated with 0.100 mol dm^{-3} sodium hydroxide solution until excess alkali has been added.

On the grid below, sketch the titration curve you would expect for this reaction.



(4)

(b) Equal volumes of 0.500 mol dm^{-3} methanoic acid and 0.250 mol dm^{-3} sodium methanoate solution are mixed to make a buffer solution.

(i) Define the term **buffer solution.**

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(2)

(ii) Calculate the pH of this buffer solution.

(3)

(iii) Explain, with the aid of equations, how this mixture acts as a buffer solution.

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(4)
(Total 13 marks)

25. One step in the manufacture of nitric acid is the reaction between nitrogen(II) oxide and oxygen to form nitrogen(IV) oxide.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -114 \text{ kJ mol}^{-1}$$

(a) (i) Use the equation to suggest the sign of ΔS_{system} for the forward reaction. Justify your answer.

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(2)

(ii) What is the sign of $\Delta S_{surroundings}$ for the forward reaction? Justify your answer.

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(2)

(b) (i) Write the expression for K_p for this reaction.
What are the units of K_p in this reaction?

Units .....

(2)

(ii) Suggest how the temperature and pressure could be altered to make nitrogen(IV) oxide more economically. Justify your suggestions by considering both yield and rate.

Temperature

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Pressure

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(4)

(c) (i) What property would allow you to follow the progress of this reaction? Justify your answer.

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(2)

(ii) In a series of experiments, the following results were obtained.

Experiment	[NO(g)] /mol dm^{-3}	[O_2(g)] /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	1.0×10^{-3}	1.0×10^{-3}	8.0×10^{-6}
2	2.0×10^{-3}	1.0×10^{-3}	3.2×10^{-5}
3	2.0×10^{-3}	2.0×10^{-3}	6.4×10^{-5}

- What is the order of the reaction with respect to NO(g)? Justify your answer.

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(2)

- What is the order of the reaction with respect to O_2(g)?

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(1)

(iii) What is the rate equation for this reaction?

(1)

(iv) What is the overall order for this reaction?

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(1)

(v) Calculate the rate constant, *k*, for this reaction. Include units with your answer.

(2)

(d) Suggest why this reaction takes place quickly at room temperature and pressure.

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(1)

(Total 20 marks)

26. (a) (i) Calculate the pH of 0.050 mol dm^{-3} hydrochloric acid.

(1)

(ii) Calculate the concentration of hydroxide ions, in mol dm^{-3}, in this solution.
At this temperature, $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.

(1)

(b) Phosphoric(V) acid, H_3PO_4, is a weak acid, forming the following equilibrium in water:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$$

(i) Write an expression for the acid dissociation constant, K_a, for phosphoric(V) acid.

(1)

(ii) Given that a 0.500 mol dm^{-3} solution of phosphoric(V) acid has a pH of 1.20, calculate the value of K_a, stating its units.
Assume that there is no further dissociation of the $H_2PO_4^-$ ion.

(4)

(c) The $H_2PO_4^-$ ion formed when phosphoric(V) acid is added to water can dissociate further into HPO_4^{2-}.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$

....

(i) In the spaces below the equation, identify the acid base conjugate pairs.

(2)

(ii) Explain why very little dissociation of the $H_2PO_4^-$ ion occurs in solutions of phosphoric(V) acid.

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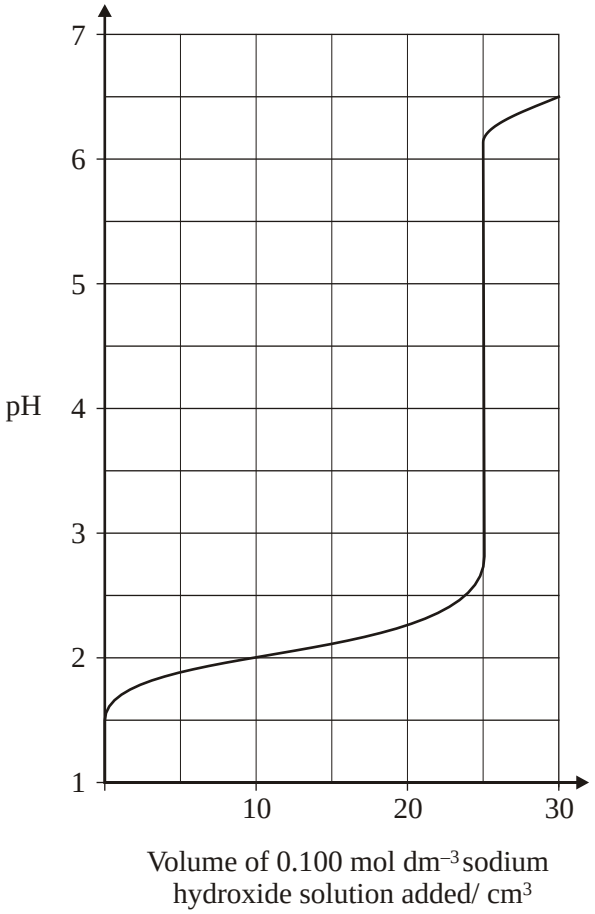
(1)

(d) The change in pH when 25.0 cm^3 of 0.100 mol dm^{-3} phosphoric(V) acid is titrated with sodium hydroxide solution of the same concentration can be seen on the graph below.



From the list below, select a suitable indicator for this titration. Justify your choice.

	pK_{In}
bromocresol green	4.7
bromothymol blue	7.0
phenolphthalein	9.3

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(2)
(Total 12 marks)

27. Dichloroethanoic acid reacts with pent-1-ene as shown by the following equation:

$$CHCl_2CO_2H(l) + C_5H_{10}(l) \rightleftharpoons CHCl_2CO_2C_5H_{11}(l)$$

(a) Give the name of the product of this reaction and also the name for the new functional group it contains.

.....

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(2)

(b) In an experiment to determine the equilibrium constant, 1.00 mol of dichloroethanoic acid was mixed with 2.30 mol of pent-1-ene. The total volume remained at 300 cm^3 throughout. When equilibrium had been reached, it was found that 0.40 mol of dichloroethanoic acid was left.

(i) List the steps in the experiment you would carry out to determine the concentration of dichloroethanoic acid present at equilibrium.

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(4)

(ii) Give the expression for the equilibrium constant, K_c, for this reaction.

(1)

(iii) Complete the table for the number of moles and concentrations at equilibrium.

Substance	Number of moles at start	Number of moles at equilibrium	Concentration at equilibrium /mol dm^{-3}
$CHCl_2COOH$	1.00	0.40	1.33
C_5H_{10}	2.30		
$CHCl_2COOC_5H_{11}$	0		

(3)

(iv) Calculate the value of K_c, and give its units.

(3)
(Total 13 marks)

28. (a) Define the term **standard enthalpy of formation**.

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(3)

(b) In the Haber process, ammonia is manufactured from nitrogen and hydrogen as shown in the equation.

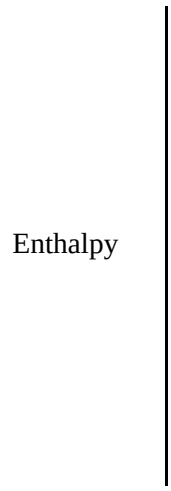
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Use the bond enthalpies below to calculate the standard enthalpy of formation of ammonia.

Bond	**Bond enthalpy / kJ mol^{-1}**
N≡N in N^2	+945
H–H in H^2	+436
N–H in NH^3	+391

(4)

(ii) Draw a labelled enthalpy level diagram for the formation of ammonia in the Haber process.



(2)

(iii) State the temperature used in the Haber process and explain in terms of the rate of reaction and position of equilibrium, why this temperature is chosen.

Temperature .....

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(3)

(iv) Identify the catalyst used in the Haber process and state what effect, if any, it has on the equilibrium yield of ammonia.

Catalyst .....

Effect on yield .....

(2)

(v) Explain why it is necessary to use a catalyst in this process.

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(1)

(c) The pressure used in the Haber process is 250 atmospheres.

(i) State and explain an advantage of increasing the pressure to 1000 atmospheres.

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(2)

(ii) Suggest a disadvantage of using a pressure of 1000 atmospheres.

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(1)

(Total 18 marks)

29. (a) Methanoic acid, HCOOH, is a weak acid. Explain what is meant by the terms **weak** and **acid**.

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(2)

(b) Write a balanced equation, including state symbols, for the reaction between aqueous solutions of methanoic acid and sodium carbonate.

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(2)

(c) The following equilibrium is set up when methanoic acid dissociates in water:

$$HCOOH(aq) + H_2O(1) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$$

(i) There are two conjugate acid-base pairs in the above equation.

Identify them by completing the sentences below:

Formula of one acid is ..... .

The formula of its conjugate base is ..... .

(1)

Formula of the other acid is ..... .

The formula of its conjugate base is ..... .

(1)

(ii) Write the expression for the acid dissociation constant, K_a, for methanoic acid.

(1)

(iii) Calculate the pH of a 0.100 mol dm^{-3} solution of methanoic acid at 298 K.

[K_a for methanoic acid is 1.60×10^{-4} mol dm^{-3} at 298 K]

(3)

(d) A buffer solution is made up by mixing equal volumes of 0.100 mol dm^{-3} methanoic acid and 0.400 mol dm^{-3} sodium methanoate.

(i) Calculate the pH of the buffer solution obtained.

(3)

(ii) Explain why the pH of this mixture of methanoic acid and sodium methanoate remains almost constant when a small quantity of an acidic solution, containing hydrogen ions, or a small quantity of an alkaline solution, containing hydroxide ions, is added.

In your explanation include equations to show the effect of adding hydrogen ions and of adding hydroxide ions.

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(3)
(Total 16 marks)

30. One stage in the manufacture of sulphuric acid is

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

The equilibrium constant $K_p = \dfrac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}}$

(a) 10.0 mol of SO_2 and 5.00 mol of O_2 were allowed to react. At equilibrium, 90.0% of the SO_2 was converted into SO_3.

(i) Calculate the number of moles of SO_2, O_2 and SO_3 present in the equilibrium mixture.

(2)

(ii) Calculate the mole fractions of SO_2, O_2 and SO_3 at equilibrium.

(1)

(iii) Assuming that the total pressure of the equilibrium mixture was 2.00 atm, calculate the partial pressures of SO_2, O_2 and SO_3 at equilibrium.

(1)

(iv) Calculate the value of K_p.

(2)

(b) The reaction between sulphur dioxide and oxygen is exothermic.

(i) State the effect, if any, on K_p of increasing the temperature at constant pressure.

.....

(1)

(ii) Use your answer to (i), **and** the expression $K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}}$ to explain the effect on the position of equilibrium of increasing the temperature at constant pressure.

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(2)

(c) The reaction was repeated at a higher pressure whilst maintaining a constant temperature.

(i) State the effect, if any, of an increase in the total pressure on the value of K_p.

.....

(1)

(ii) State the effect, if any, of this increase in pressure on the amount of sulphur trioxide in the equilibrium mixture.

.....

(1)

(d) State the effect, if any, of a catalyst on:

(i) K_p

.....

(1)

(ii) the equilibrium position.

.....

(1)

(Total 13 marks)

31. (a) What is the formula of the ion found in all acidic solutions?

.....

(1)

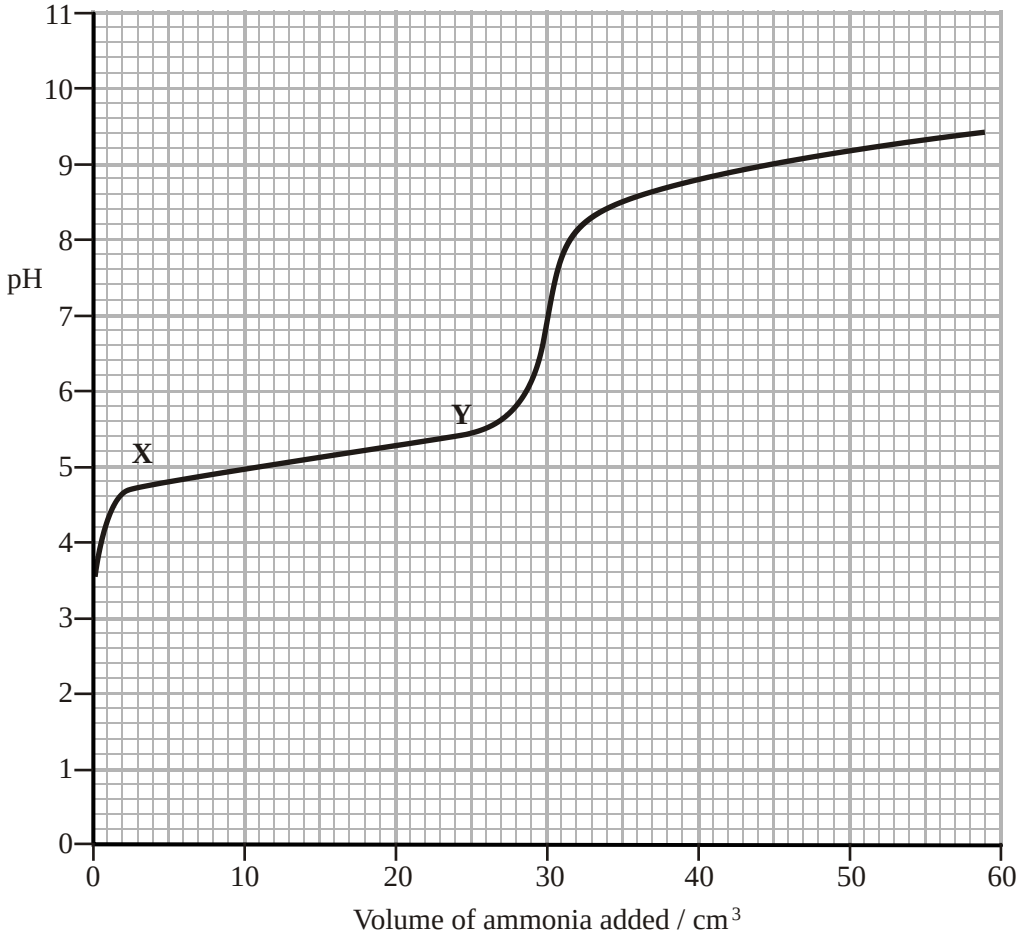
(b) Which of the following substances would form an acidic solution in water?

A CH_4 B NaOH C HCO_2H
D NH_3 E HNO_3

.....

(2)
(Total 3 marks)

32. 10.0 cm^3 of a solution of butanoic acid, $CH_3CH_2CH_2CO_2H$, of concentration 0.00660 mol dm^{-3}, was titrated with a solution of aqueous ammonia using a pH probe.
The pH was recorded throughout, and the results were plotted as shown below.



(a) (i) Using the pH of butanoic acid from the graph, calculate the initial hydrogen ion concentration.

(2)

(ii) Write the expression for the acid dissociation constant, K_a, for an aqueous solution of butanoic acid.

(1)

(iii) Calculate the value of K_a making the usual assumptions. Give your answer to **two** significant figures.

(2)

(b) (i) Write an equation for the reaction between butanoic acid and ammonia. State symbols are **not** required.

(1)

(ii) Name the **two** compounds, apart from water, which are present in the mixture between **X** and **Y** shown on the graph.

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(2)

(iii) What **type** of mixture is present between **X** and **Y**? What evidence is there for your answer by reference to the graph?

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(2)

(iv) Explain why it is **not** possible to carry out this titration using an indicator.

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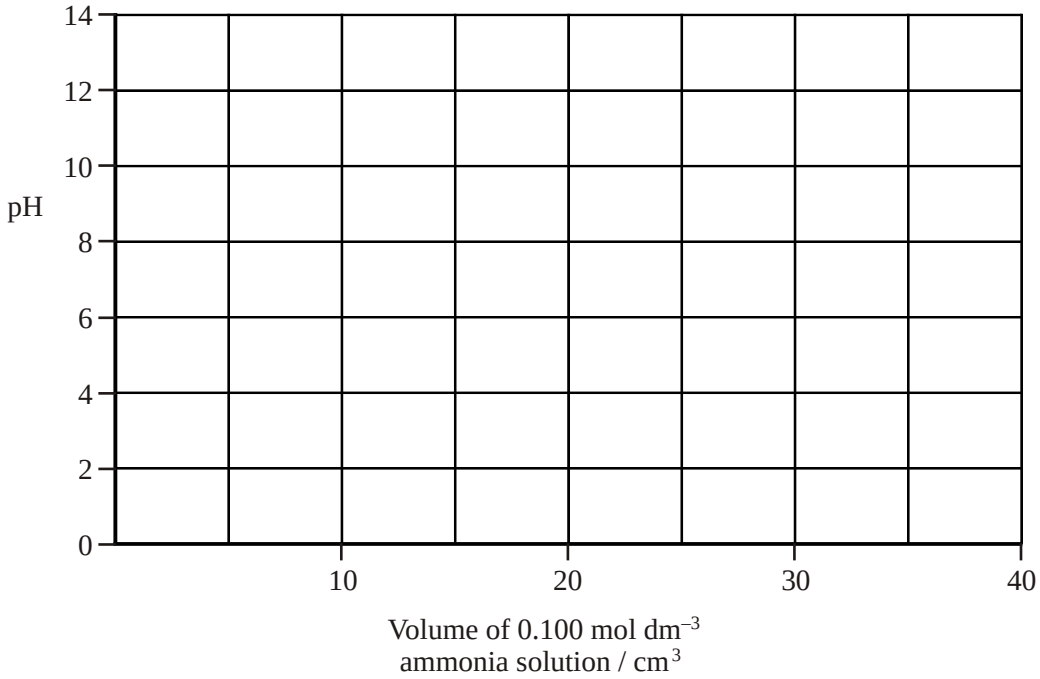
(1)

(v) Use the graph to estimate the end-point of the titration. Hence calculate the concentration of the ammonia solution.

(2)
(Total 13 marks)

33. (a) Sketch the titration curve that you would expect if 25.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid, HCl, is titrated with 40.0 cm^3 of 0.100 mol dm^{-3} ammonia solution, NH^3.



(4)

(b) Using your answer to (a), select a suitable indicator for this titration. Put a tick in the appropriate box in the table below.

Indicator	pK_{Ind}	(✓)
thymol blue	1.7	
bromocresol green	4.7	
phenol red	7.9	
phenolphthalein	9.3	

(1)

(c) Suggest why there is no suitable indicator for the titration of ethanoic acid with ammonia.

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(2)

(Total 7 marks)

34. Methanoic acid and ethanol react together to form ethyl methanoate, $HCOOC_2H_5$, and water. This reaction is reversible and can be allowed to reach equilibrium.

$$HCOOH(l) + C_2H_5OH(l) \rightleftharpoons HCOOC_2H_5\ (l) + H_2O(l) \qquad \Delta H = +45\ kJ\ mol^{-1}$$

(a) Draw the **full** structural formula of ethyl methanoate, showing all bonds.

(1)

(b) What type of organic compound is ethyl methanoate?

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(1)

(c) In an experiment, 3.00 mol methanoic acid, HCOOH, and 6.25 mol ethanol, C_2H_5OH, were mixed together. A small quantity of catalyst was added. The mixture was left for several days in a water bath to reach equilibrium at constant temperature.

(i) Complete the table.

Number of moles in the reaction mixture				
	HCOOH	C_2H_5OH	$HCOOC_2H_5$	H_2O
at start of experiment	3.00	6.25	0.00	0.00
at equilibrium	0.50			

(2)

(ii) Write an expression for the equilibrium constant, K_c, for the reaction.

(1)

(iii) Calculate K_c for the reaction at the temperature of the experiment. The total volume of the equilibrium mixture was 485 cm^3.

(2)

(iv) State and explain whether K_c for this reaction has units.

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(1)

(d) (i) The temperature of this equilibrium mixture is **lowered**.

Explain the effect of this on the value of the equilibrium constant and **hence** on the yield of ethyl methanoate.

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(4)

(ii) A student added more catalyst to the mixture.

State, giving a reason, what would happen to the composition of the equilibrium mixture.

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(1)

(Total 13 marks)

35. When solid lead(II) sulphate is added to a solution of sodium iodide, the following equilibrium is established:

$$PbSO_4(s) + 2I^-(aq) \rightleftharpoons PbI_2(s) + SO_4^{2-}(aq)$$

The equilibrium constant, *K*c, for this reaction may be found by adding an excess of solid lead(II) sulphate to a known volume of a standard solution of sodium iodide. The mixture is left to reach equilibrium at a constant temperature, *T*.

Ice-cold water is added to freeze the position of equilibrium and the mixture is then titrated with standard silver nitrate solution.

In a typical experiment, excess lead(II) sulphate was added to 50.0 cm^3 of 0.100 mol dm^{-3} sodium iodide solution. The whole equilibrium mixture required 31.0 cm^3 of 0.100 mol dm^{-3} silver nitrate solution to react with the aqueous iodide ions.

The expression for K_c for this reaction is

$$K_c = \frac{[SO_4^{2-}]}{[I^-]^2}$$

(a) Why is it **not** necessary to know the mass of the lead(II) sulphate used in the experiment?

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(1)

(b) Give the ionic equation for the reaction between silver nitrate solution and aqueous iodide ions to produce a precipitate of silver iodide, AgI.

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(1)

(c) From the data given above, calculate the equilibrium amounts of the iodide and of the sulphate ions in solution. Hence calculate the equilibrium concentration of these ions, and the value of K_c for the reaction at temperature T, including the units, if any.

(8)
(Total 10 marks)

36. This question concerns the reactions of some compounds of nitrogen.

(a) The ammonium ion reacts with water and behaves as an acid.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

(i) Identify the TWO conjugate acid-base pairs in the spaces provided.

acid 1 ..... base 1 .....

acid 2 ..... base 2 .....

(1)

(ii) Write the expression for the acid dissociation constant, K_a, of the ammonium ion.

(1)

(iii) A solution of ammonium chloride has a pH of 5.00 at 25°C.
K_a for the ammonium ion is 5.62×10^{-10} mol dm^{-3} at 25°C.

Calculate the concentration of this solution. State any assumptions you have made.

(4)

(iv) Use the following table and your answer from part (iii) to suggest a suitable indicator for the titration of ammonia solution with hydrochloric acid. Justify your answer.

Indicator	**pK_{In}**
thymol blue	1.7
methyl red	5.1
phenolphthalein	9.3

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(2)

(b) Hydrogen cyanide is a weak acid in aqueous solution.

Write an equation to show why aqueous solutions of cyanide ions are alkaline.

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(1)

(c) Hydrogen cyanide reacts with propanal as follows:

$$CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$$

Propanal is reacted with a solution of potassium cyanide, KCN, containing a little dilute sulphuric acid.

(i) What **type** of reaction is this?

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(1)

(ii) Give the mechanism for the reaction.

(3)

(iii) It is important that the pH is neither too acidic nor too alkaline if a good yield of the product is to be obtained. Explain why this is so.

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(2)

(d) In an investigation of the kinetics of the nucleophilic substitution reaction between 1-chloropropane and potassium cyanide in aqueous ethanolic solution, the reaction was found to be first order with respect to 1-chloropropane and first order with respect to cyanide ions.

(i) Give the rate equation for the reaction.

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(1)

(ii) Write a mechanism for the reaction that is consistent with this rate equation.

(3)
(Total 19 marks)

37. Ammonia can be oxidised to form nitrogen(II) oxide and water according to the equation

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H^{\ominus} = -905.6 \text{ kJ mol}^{-1}.$$

In industry, the reaction is carried out at 1123 K with a platinum/rhodium catalyst.

The standard entropy of one mole of each substance in the equation, measured at 298 K, is shown in the table below.

Substance	$S^{\ominus}$/ J mol^{-1} K^{-1}
NH_3 (g)	+192.3
O_2 (g)	+205.0
NO (g)	+210.7
H_2O (g)	+188.7

(a) (i) Use the values given to calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction. Include the sign and units in your final answer.

(2)

(ii) Is the sign for your value for $\Delta S^{\ominus}_{system}$ what you expected? Justify your answer.

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(1)

(iii) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 1123 K for this reaction. Include the sign and units in your final answer.

(2)

(iv) Calculate the total entropy change, ΔS_{total}, for this reaction at 1123 K. Include the sign and units in your final answer. You may assume that ΔS_{system} is unchanged at high temperatures.

(1)

(v) What does your answer to (iv) tell you about the extent of the reaction at 1123 K? Justify your answer.

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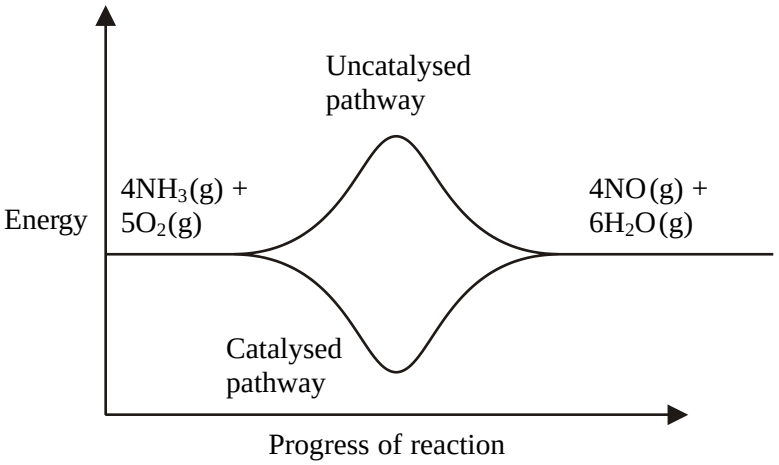
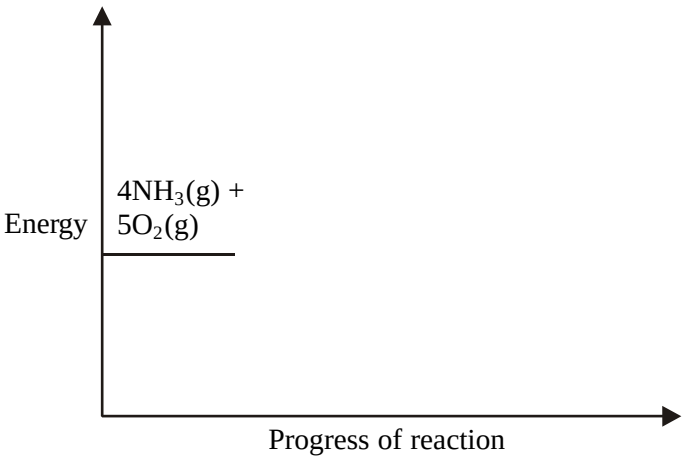
(1)

(vi) An energy profile was proposed to illustrate the effect of the catalyst on this reaction. The proposal has two errors. Draw a corrected version on the axes below.

Proposal



Corrected version



(2)

(b) The oxidation of nitrogen(II) oxide leads to the following equilibrium

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

The number of moles of each gas in a reaction mixture at equilibrium, at a pressure of 1.5atm, was found to be

Substance	Number of moles at equilibrium
NO (g)	0.025
O_2 (g)	0.025
NO_2 (g)	4.95

(i) Write the expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) Calculate the mole fraction of each gas and hence the value of the equilibrium constant, K_p, for this mixture. Include units, if required, in your answer.

(4)

(iii) What does your answer to (ii) tell you about the position of the equilibrium? Justify your answer.

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(1)

(iv) If the total pressure of the reaction mixture was increased, describe what would happen to the value of the equilibrium constant, K_p, and the partial pressure of $NO_2(g)$. In each case justify your answer.

Equilibrium constant, K_p.

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Partial pressure of $NO_2(g)$.

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(2)

(Total 17 marks)

38. (a) The table below shows the acid dissociation constants, K_a, of three carboxylic acids.

Acid	Structural formula	K_a/ mol dm^{-3}
Chloroethanoic	CH_2ClCO_2H	1.3×10^{-3}
Dichloroethanoic	$CHCl_2CO_2H$	5.0×10^{-2}
Trichloroethanoic	CCl_3CO_2H	2.3×10^{-1}

(i) Write an expression for the acid dissociation constant, K_a, of chloroethanoic acid.

(1)

(ii) Calculate the pH of a 0.0010 mol dm^{-3} solution of chloroethanoic acid, making the usual assumptions.

(3)

(iii) Which acid would have the lowest pH at a concentration of 0.0010 mol dm^{-3}? Use both the data and the structure of the acids to justify your answer. No further calculation is required.

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(2)

(b) Chloroethanoic acid, CH_2ClCO_2H, reacts with methanol, CH_3OH, in the presence of a sulphuric acid catalyst.

(i) Draw the **displayed** formula and give the name of the **organic** product formed.

Displayed Formula

Name .....

(3)

(ii) What name is given to the functional group formed in this organic product?

.....

(1)

(iii) What type of reagent is methanol in this reaction? Explain why it is able to behave in this way and describe how it attacks the chloroethanoic acid.
You may find it helpful to draw a diagram.

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(3)

(iv) How would you convert the organic product of the reaction between chloroethanoic acid and methanol back into the original compounds?

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(2)
(Total 15 marks)

39. This question is about ammonia, NH3, which is produced as shown in the following equation.

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

(a) Use oxidation numbers to explain why this is a redox reaction.

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(2)

(b) (i) Use the average (mean) bond enthalpy data to calculate a value for the enthalpy change for this reaction. You are reminded to show **all** your working.

Bond	Average bond enthalpy / kJ mol^{-1}
N≡N	944
H—H	436
N—H	388

(3)

(ii) The actual standard enthalpy change for this reaction is –92 kJ mol^{-1}. Explain why the value you calculated in (b)(i) is not the same as this.

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(1)

(iii) At room temperature, a mixture of nitrogen and hydrogen is thermodynamically unstable with respect to ammonia, but is kinetically stable.

Use the data in (b)(i) and (ii) to help you explain why this mixture is

thermodynamically unstable

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kinetically stable

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(3)

(c) The manufacturer of ammonia would like to achieve a high rate of reaction and a high equilibrium yield of product.

(i) State and explain, in terms of collision theory, TWO ways to increase the rate of the reaction. An increase in pressure does **not** alter the rate in this process.

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(6)

(ii) State and explain TWO ways to increase the equilibrium yield of ammonia.

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(4)
(Total 19 marks)

40. (a) The equilibrium between hydrogen iodide, hydrogen and iodine was investigated by sealing hydrogen iodide in glass tubes and heating the tubes at 698 K until equilibrium was reached.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H = +\ 9.4\ kJ\ mol^{-1}$$

The glass tubes were cooled rapidly and then opened in a solution of potassium iodide so that the concentration of iodine at equilibrium could be determined by titration.

(i) Suggest why the reaction mixture was **cooled rapidly**.

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(2)

(ii) The expression for the equilibrium constant, K_c, for the above reaction is

$$K_c = \frac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$$

One of the tubes was found to contain iodine at a concentration of 5.0×10^{-4} mol dm^{-3}.

Calculate the equilibrium concentration of hydrogen iodide, in mol dm^{-3}.
The equilibrium constant, K_c, for the above reaction is 0.019 at 698 K.

(3)

(b) In a different experiment, 1.0 mol of hydrogen and 1.0 mol of iodine were allowed to reach equilibrium at 698 K.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At equilibrium, 80% of the hydrogen was converted to hydrogen iodide at a total pressure of 1.1 atm.

(i) Write an expression for the equilibrium constant, K_p, for the reaction as shown.

(1)

(ii) Calculate the value of K_p.

(4)

(iii) Explain why, in this case, K_p has no units.

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(1)
(Total 11 marks)

41. This question is about propanoic acid, CH_3CH_2COOH.

(a) Propanoic acid is a weak acid which dissociates as follows

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

(i) In the above equation there are two conjugate acid-base pairs.

Identify them by completing the sentences below

Formula of one acid is .....

The formula of its conjugate base is .....

Formula of the other acid is .....

The formula of its conjugate base is .....

(2)

(ii) Propanoic acid is a weak acid. Explain what is meant by the term **weak acid**.

Weak

.....

.....

Acid

.....

.....

(2)

(b) The acid dissociation constant, K_a, for propanoic acid is 1.30×10^{-5} mol dm^{-3} at 298 K.

(i) Write the expression for the acid dissociation constant, K_a, for propanoic acid.

(1)

(ii) A solution of propanoic acid has a pH of 3.44 at a temperature of 298 K.

Calculate the concentration, in mol dm^{-3}, of the propanoic acid solution. Show clearly **two** assumptions you have made.

Calculation:

Assumptions:

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(5)

(c) A mixture of sodium propanoate and propanoic acid acts as a buffer solution.

(i) What is meant by a **buffer solution**?

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(2)

(ii) Calculate the pH of a buffer solution made by mixing 100 cm^3 of 0.0100 mol dm^{-3} propanoic acid solution with 300 cm^3 of 0.00500 mol dm^{-3} sodium propanoate solution at 298 K.

[K_a for propanoic acid is 1.30×10^{-5} mol dm^{-3} at 298 K]

(3)
(Total 15 marks)

42. The equation below shows the equilibrium existing between nitrogen, oxygen and nitrogen monoxide.

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

The equilibrium constant, K_p, at 298 K is 5.0×10^{-31}

(a) (i) Write an expression for the equilibrium constant, K_p, in terms of the partial pressures of the three gases.

(1)

(ii) Why does the value for K_p have no units?

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(1)

(b) An equilibrium mixture of these three gases was found to contain nitrogen, at a partial pressure of 0.87 atm, and oxygen, at a partial pressure of 0.23 atm.

(i) Calculate the partial pressure exerted by the nitrogen monoxide.

(2)

(ii) Deduce the value of the total pressure of the equilibrium mixture of gases.

(1)

(iii) Assuming that the total pressure on the mixture of gases is doubled, what, if any, would be the effect on the

- partial pressure of nitrogen monoxide

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.

- equilibrium constant, K_p?

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(2)

(c) Inside a car engine, air (a mixture of nitrogen and oxygen) is drawn in and, under the high temperatures operating, the value of K_p increases dramatically.

This increase is also accompanied by an increase in the value of ΔS_{total}. Typical values of K_p and ΔS_{total} are shown in the table below.

Temperature / K	K_p	ΔS_{total} / J mol^{-1} K^{-1}
298	5.0×10^{-31}	–580
1500	1.0×10^{-5}	– 96

Although the value of ΔS_{system} is unlikely to alter very much, the value for $\Delta S_{surroundings}$ will change significantly.

(i) At a temperature of 1500 K, ΔS_{total} is negative.

Does this mean that the reaction between nitrogen and oxygen cannot occur at this temperature? Explain your reasoning.

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(1)

(ii) Why is the value for ΔS_{system} for this equilibrium approximately constant when the temperature rises above 298 K?

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(1)

(iii) What is the sign of $\Delta S_{surroundings}$ for an **endothermic** reaction? Justify your answer.

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(1)

(iv) Explain why an endothermic reaction results in an increase in the value of ΔS_{total} as the temperature increases.

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(1)

(d) A student used the value for K_p at 1500 K to calculate the partial pressure of nitrogen monoxide inside a working car engine.

Why might the actual partial pressure be lower than the calculated answer?

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(1)

(Total 12 marks)

43. Calculate the pH of the buffer solution formed by mixing 10 cm^3 of aqueous benzoic acid of concentration 0.010 mol dm^{-3} with 40 cm^3 of aqueous sodium benzoate of concentration 0.020 mol dm^{-3}.

For benzoic acid, the acid dissociation constant, K_a, is 6.3×10^{-5} mol dm^{-3}.

You may find it helpful to use the relationship $pH = -\log Ka - \log \frac{[acid]}{[base]}$

(Total 3 marks)

44. Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +58 \text{ kJ mol}^{-1}$$

(a) Write the expression for the equilibrium constant, K_p, for the above reaction.

(1)

(b) (i) An equilibrium mixture contains a mole fraction of dinitrogen tetroxide, $N_2O_4 = 0.20$, and nitrogen dioxide, $NO_2 = 0.80$. The total pressure of this mixture is 1.1 atm.

Calculate K_p at this temperature, stating its units.

(3)

(ii) Calculate the total pressure required to reduce the mole fraction of N_2O_4 to 0.10.

(3)

(c) (i) What is the effect on K_p, if any, of raising the temperature?

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(1)

(ii) Use your answer to (c)(i) to explain the effect of increasing the temperature on the position of equilibrium.

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(2)
(Total 10 marks)

45. (a) The values of the ionic product of water, *K*w, at two different temperatures are shown in the table below.

Temperature /°C	K_w / $mol^2\ dm^{-6}$
25	1.00×10^{-14}
50	5.48×10^{-14}

(i) Write an equation to represent the ionisation of water.

.....

(1)

(ii) Write the expression for K_w.

.....

(1)

(iii) Define the term **pH**.

.....

.....

(1)

(iv) Calculate the pH of pure water **at 50 °C**.

(2)

(v) Explain why pure water at 50 °C is neutral despite the fact that its pH is not 7.

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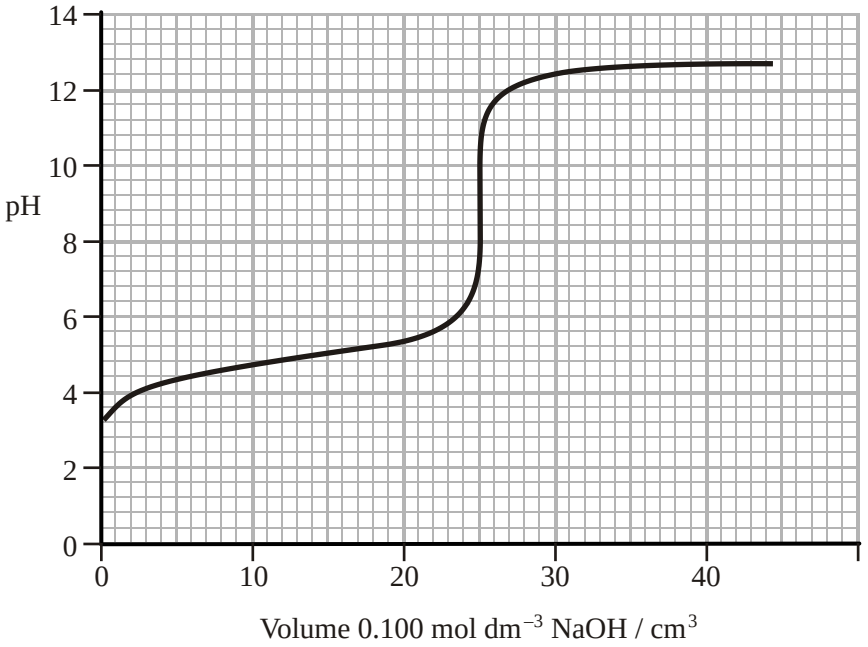
(1)

(b) The pH curve shown below was obtained when a 0.100 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of a 0.100 mol dm^{-3} solution of ethanoic acid.



(i) What volume of sodium hydroxide solution is required to neutralise half of the ethanoic acid in this reaction?

Volume added = ...cm^3

(1)

(ii) Use the graph to determine the pH when the volume of sodium hydroxide you have stated in part (i) has been added.

pH is .....

(1)

(iii) Write an expression for the acid dissociation constant, K_a, of ethanoic acid, CH_3COOH.

(1)

(iv) Use your answers to parts (ii) and (iii) to determine the value of K_a for ethanoic acid at the temperature of the titration. Give your answer to **two** significant figures.

(2)

(c) Phenolphthalein is a suitable indicator for a titration between ethanoic acid and sodium hydroxide solutions whereas methyl orange is **not** a suitable indicator.

Explain why this is so.

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(2)
(Total 13 marks)

46. Phosphorus(V) chloride dissociates as follows:

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g) \qquad \Delta H^{\ominus} = + 123.8 \text{ kJ mol}^{-1}$$

Substance	Standard entropy, $S^{\ominus}$ / J mol^{-1} K^{-1}
$PCl_5(s)$	+ 166.5
$PCl_3(l)$	+ 217.1
$Cl_2(g)$	+ 165.0

(a) (i) Explain why the entropy of solid phosphorus(V) chloride, PCl_5, is smaller than the entropy of liquid phosphorus(III) chloride, PCl_3?

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(1)

(ii) Calculate $\Delta S^{\ominus}_{system}$ for the forward reaction. Include a sign in your answer.

(1)

(iii) Is the sign of $\Delta S^{\ominus}_{system}$ as you would expect? Fully justify your answer.

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(2)

(b) Calculate $\Delta S^{\ominus}_{surroundings}$ for the forward reaction at 298 K. Include a sign and units in your answer.

(2)

(c) (i) Use your answers to calculate $\Delta S^{\ominus}_{total}$ for the forward reaction at 298 K. Include a sign in your answer.

(1)

(ii) Comment on the position of equilibrium at 298 K.

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(1)

(d) In an experiment to investigate this equilibrium, 41.7 g of phosphorus(V) chloride (molar mass 208.5 g mol^{-1}) was heated in a closed vessel at 150 °C until equilibrium was established. The final pressure was found to be 4.32 atm and 0.15 moles of phosphorus(V) chloride remained. At this temperature all of the reactants and products are gaseous.

(i) Give the expression for the equilibrium constant, K_p, and its units at this temperature.

(2)

(ii) Complete the table

Substance	Moles at start	Moles at equilibrium	Partial pressure at equilibrium, p_{eq} /atm
$PCl_5(g)$		0.15	
$PCl_3(g)$	0		
$Cl_2(g)$	0		
Total number of moles at equilibrium			

(3)

(iii) Calculate K_p.

(1)

(iv) How would you expect the value of K_p to change, if at all, if the following changes were made? Justify each of your answers.

A Only 20.85 g of phosphorus(V) chloride had been used.

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B The temperature had been increased to 250 °C.

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(2)

(Total 16 marks)

47. Human blood plasma is a buffer solution. It partly owes its buffer properties to carbon dioxide, produced by respiration, dissolving in the blood for transportation to the lungs.

Carbon dioxide dissolves in water establishing the equilibrium

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

(a) (i) Write the expression for *K*a for this equilibrium and give its units.

Units .....

(2)

(ii) What is the relationship between pK_a and K_a?

(1)

(b) Explain what is meant by a buffer solution.

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(2)

(c) $HCO_3^-(aq)$ can act as an acid or a base.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

In this equilibrium, decide whether $HCO_3^-(aq)$ is acting as an acid or as a base. Give the reason for your decision.

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(1)

(d) A sprinter had the pH and total carbonate concentration, $[CO_2 + HCO_3^-]$, of his blood plasma measured immediately before and after a race. The following results were obtained.

	pH	Total carbonate concentration, $[CO_2 + HCO_3^-]$ / mol dm^{-3}
Before race	7.4	2.52×10^{-2}
After race	7.3	1.98×10^{-2}

The pH of a buffer solution is given by the equation

$$pH = pK_a - \log \frac{[acid]}{[base]}$$

For this equilibrium pK_a is 6.5.

(i) Use this information, together with the data in the table, to calculate $\frac{[\text{acid}]}{[\text{base}]}$ before the race.

(2)

(ii) The concentration of HCO_3^- is 0.0224 mol dm^{-3}. Calculate the concentration of CO_2 before the race.

(1)

(iii) Use your results from (d)(i) and (ii) to complete the table below which will allow you to compare the results before and after the race.

	$\frac{[\text{acid}]}{[\text{base}]}$	$[HCO_3^-]$ / mol dm^{-3}	$[CO_2]$ / mol dm^{-3}
Before race		0.0224	
After race	0.158	0.0171	0.00270

Two hypotheses have been proposed to explain why vigorous exercise results in an increase in blood plasma acidity (from 7.4 to 7.3).

Greater muscle activity during a race requires:

either

Hypothesis I the combustion of larger quantities of glucose, resulting in an increase in dissolved carbon dioxide and hence an increase in acidity.

or

Hypothesis II partial oxidation of glucose to lactic acid and hence an increase in acidity.

State, giving your reasons, which hypothesis is favoured by the data and your calculations.

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(2)
(Total 11 marks)

48. For the equilibrium,

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

Which is the correct expression for K_p?

A $\dfrac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$

B $\dfrac{P_{N_2(g)}P_{H_2(g)}}{P_{NH_3(g)}}$

C $\dfrac{P^2{}_{NH_3(g)}}{P_{N_2(g)}P^3{}_{H_2(g)}}$

D $\dfrac{P_{N_2(g)}P^3{}_{H_2(g)}}{P^2{}_{NH_3(g)}}$

(Total 1 mark)

49. The expression for *K*c for the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

What are the units of *K*c in this equilibrium expression?

A mol dm^{-3}

B mol^2 dm^{-6}

C dm^3 mol^{-1}

D atm^{-1}

(Total 1 mark)

50. For the equilibrium

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

which one of the following changes would result in a different value of the equilibrium constant?

A an increase in temperature

B a decrease in pressure

C an increase in pressure

D an increase in the concentration of $NO_2(g)$

(Total 1 mark)

51. Solutions of concentration 0.1 mol dm^{-3} of iron(II) ions and silver(I) ions were mixed at room temperature and allowed to reach equilibrium.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Which one of the following statements is true?

A as the equilibrium position was approached, the forward reaction became slower until it stopped.

B at the equilibrium position, no more Ag(s) reacted with $Fe^{3+}(aq)$.

C at the equilibrium position, the rate of the forward reaction equalled the rate of the backward reaction.

D no $Fe^{3+}(aq)$ reacted with Ag(s) until the equilibrium position was reached.

(Total 1 mark)

52. This question concerns four solutions, A to D. They were prepared by mixing equal volumes of 0.2 mol dm^{-3} solutions of two different substances. The substances were

A HCl(aq) and NaOH(aq)

B HCl(aq) and NaCl(aq)

C $NH_3(aq)$ and $NH_4Cl(aq)$

D $CH_3COOH(aq)$ and $CH_3CO_2Na(aq)$

Select, from **A** to **D**, the mixture which would:

(a) have the lowest concentration of hydrogen ions

A

B

C

D

(1)

(b) act as a buffer of pH about 5

A

B

C

D

(1)

(c) have a chloride ion concentration of 0.2 mol dm^{-3}.

A

B

C

D

(1)
(Total 3 marks)

53. This question concerns the titration of a solution of sodium hydroxide with a solution of hydrochloric acid. As the titration proceeds the pH of the mixture changes.

(a) What was the pH when 24.95 cm^3 of 1.00 mol dm^{-3} NaOH(aq) had been added to 25 cm^3 of 1.00 mol dm^{-3} HCl(aq)?

A 3

B 6

C 8

D 11

(1)

(b) What was the pH when 25.05 cm^3 of 1.00 mol dm^{-3} NaOH(aq) had been added to 25 cm^3 of 1.00 mol dm^{-3} HCl(aq)?

A 3

B 6

C 8

D 11

(1)

(c) Which one of the following indicators would be **most** suitable to use to determine the end point of this titration?

		pH range
A	methyl violet	0–1.6
B	universal indicator	3–11
C	thymolphthalein	8.3–10.6
D	alizarin yellow R	10.1–13.0

(1)

(Total 3 marks)

54. This question is about the pineapple flavouring used in sweets. It is an ester with the formula $C_3H_7COOCH_3$, which can be broken down into butanoic acid and methanol when mixed with hydrochloric acid.

The following equilibrium is set up:

$$C_3H_7COOCH_3(l) + H_2O(l) \rightleftharpoons C_3H_7COOH(l) + CH_3OH(l)$$

(a) Give the name of this ester.

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(1)

(b) Why does the ester have a comparatively low boiling point compared to the other three substances in the equation?

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(1)

(c) What is the name given to this type of reaction?

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(1)

(d) Suggest the reasons why manufacturers choose to use the chemically manufactured pineapple flavouring rather than the natural product and why consumers might prefer to choose the natural product.

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(4)

(e) In an experiment, 10.2 g (0.10 mol) of the ester was mixed with 18 cm^3 of 1.0 mol dm^{-3} hydrochloric acid and left until equilibrium had been reached. The hydrochloric acid acts as a catalyst and contains 18 g (1 mol) of water. At equilibrium, 4.4 g of butanoic acid was found to be present.

Molar mass of butanoic acid = 88 g; assume the total volume at equilibrium is 30 cm^3.

Give the expression for the equilibrium constant, K_c, for this equilibrium and calculate its value. Explain why it has no units.

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(5)

(Total 12 marks)

55. Methane reacts with steam in an endothermic reaction.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(a) State the effect on the value of the equilibrium constant of an increase in temperature.

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(1)

(b) Use your answer to (a) to explain the effect of this change on the position of equilibrium.

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(2)
(Total 3 marks)

56. This question is about the reaction of magnesium with hydrochloric acid which takes place rapidly at room temperature.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad \Delta H = -467 \text{ kJ mol}^{-1}$$

(a) Rewrite the equation omitting spectator ions.

(1)

(b) Suggest the sign of the following entropy changes for this reaction. Justify each of your answers.

(i) ΔS_{system}

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(2)

(ii) $\Delta S_{surroundings}$

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(2)

(iii) ΔS_{total}

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(1)

(c) A student carried out this experiment at five different temperatures in order to calculate the activation energy of the reaction. The student's laboratory record is shown below.

Method

Clean a strip of magnesium weighing 0.100 g with sand paper. Measure the temperature of 20 cm^3 of 1.00 mol dm^{-3} hydrochloric acid in a 100 cm^3 beaker. Add the magnesium ribbon, stir continuously, and time how long it takes for the magnesium to disappear. Repeat the experiment at four other temperatures.

***Assumption**: the initial rate of reaction is proportional to 1/time.*

Results

Temperature /°C	***Temperature /K***	***1/T /K^{-1}***	***time /s***	***1/time /s^{-1}***	***ln 1/time***
24	*297*	*3.37×10^{-3}*	*45*	*0.0222*	*–3.81*
33	*306*	*3.27×10^{-3}*	*25*	*0.0400*	*–3.22*
45	*318*	*3.14×10^{-3}*	*11*	*0.0909*	*-2.40*
56	*329*	*3.04×10^{-3}*	*6*	*0.1667*	*-1.79*
10	*283*	*3.53×10^{-3}*	*122*	*0.0082*	*-4.80*

The Arrhenius equation is $\ln k = -E_a/R \times (1/T) + \text{constant}$

ln 1/time is proportional to ln k and so a graph of ln 1/time will have the same gradient as that of the Arrhenius plot of ln k against 1/Temperature

The student plotted the graph of ln 1/time against 1/Temperature and from this the activation energy, E_A, was calculated as + 51.3 kJ mol^{-1}.

(i) Suggest the reason for cleaning the magnesium ribbon with sand paper.

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(1)

(ii) Calculate the number of moles of hydrochloric acid used up when all the magnesium reacts in one experiment. Hence comment on whether the change in concentration during the reaction will have a significant effect on the validity of the assumption that the initial rate of reaction is proportional to 1/time. How would you overcome this potential error?

[Take the relative atomic mass of magnesium as 24 in this and subsequent calculations.]

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(5)

(iii) Use the value of ΔH and other information given in the question to calculate the temperature change in an experiment assuming no energy is lost to the surroundings. Hence comment on whether this change in temperature will have a significant effect. How would you overcome this potential error?

[ΔH = –467 kJ mol^{-1}.

heat produced = mass × specific heat capacity × change in temperature.

Assume that the specific heat capacity of the solution is 4.18 J K^{-1} g^{-1}]

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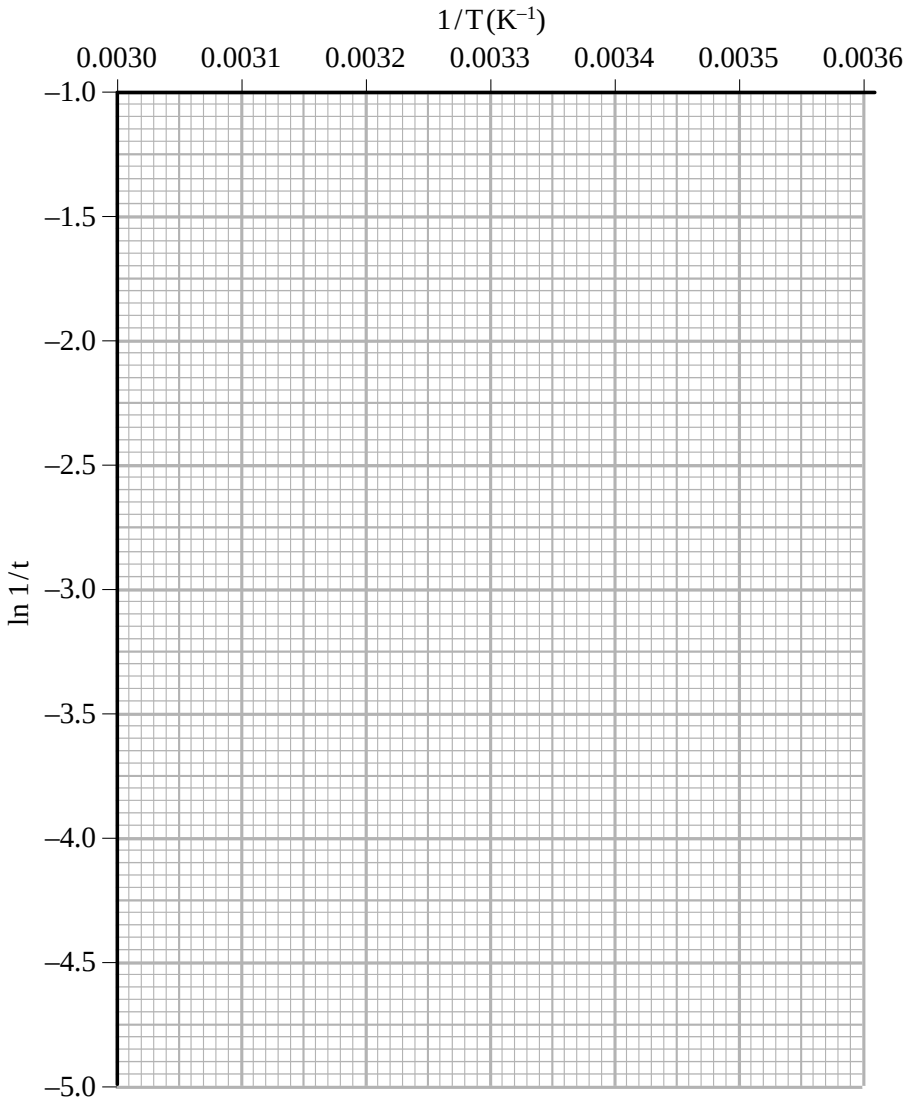
(4)

(iv) The most difficult thing to measure accurately is the time it takes for the magnesium to disappear and the time measured can be up to 2 seconds out. Assuming this error, calculate the shortest time at 56 °C **and** the longest time at 10 °C for this reaction.

Complete the table for these times. Plot the two points on the grid below and join them with a straight line. From the gradient, which equals $-E_A/R$, of this line calculate another value for the activation energy.

Temperature / °C	Temperature /K	1/T /K^{-1}	time /s	1/time /s^{-1}	ln 1/time
56	329	3.04×10^{-3}			
10	283	3.53×10^{-3}			



(v) If the reaction mixture is not stirred, the magnesium tends to float on the surface of the acid.

Suggest how this would affect the measurements of the rate of the reaction.

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(1)

(vi) Suggest **two** other improvements the student could do to this experiment to improve the accuracy or validity of the results.

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(2)

(vii) If ethanoic acid of the same concentration and at the same temperature is used instead of hydrochloric acid, explain how the rate would differ.

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(1)

(Total 24 marks)

57. One step in the production of nitric acid is the oxidation of ammonia.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

This is carried out at 900 °C over a platinum-rhodium catalyst and is an example of heterogeneous catalysis.

Explain in terms of collision frequency and collision energy how the rate would change if the temperature were increased, and which of these causes the greater effect.

What is the difference between a heterogeneous and a homogeneous catalyst? Suggest **one** advantage of using a heterogeneous catalyst in processes such as this.

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(Total 6 marks)