HL Paper 2

Consider the following reaction studied at 263 K.

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

It was found that the forward reaction is first order with respect to Cl_2 and second order with respect to NO. The reverse reaction is second order with respect to NOCl.

Consider the following equilibrium reaction.

$$Cl_2(g) + SO_2(g) \rightleftharpoons SO_2Cl_2(g) \quad \Delta H^{\ominus} = -84.5 \text{ kJ}$$

In a 1.00 dm^3 closed container, at 375 °C, 8.60×10^{-3} mol of SO_2 and 8.60×10^{-3} mol of Cl_2 were introduced. At equilibrium, 7.65×10^{-4} mol of SO_2Cl_2 was formed.

a.i. State the rate expression for the forward reaction. [1]

a.ii. Predict the effect on the rate of the forward reaction and on the rate constant if the concentration of NO is halved. [2]

a.iii. 1.0 mol of Cl_2 and 1.0 mol of NO are mixed in a closed container at constant temperature. Sketch a graph to show how the concentration of NO and NOCl change with time until after equilibrium has been reached. Identify the point on the graph where equilibrium is established. [4]

b. Consider the following reaction. [2]

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

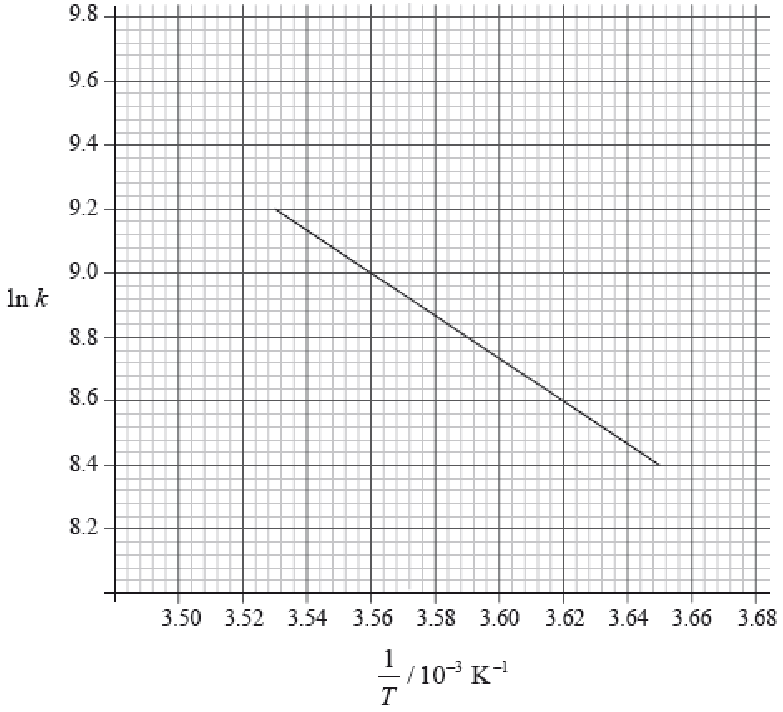
Possible reaction mechanisms are:

$$\begin{array}{lll} \text{Above 775 K:} & NO_2 + CO \rightarrow NO + CO_2 & \text{slow} \\ \text{Below 775 K:} & 2NO_2 \rightarrow NO + NO_3 & \text{slow} \\ & NO_3 + CO \rightarrow NO_2 + CO_2 & \text{fast} \end{array}$$

Based on the mechanisms, deduce the rate expressions above and below 775 K.

c. State **two** situations when the rate of a chemical reaction is equal to the rate constant. [2]

d. Consider the following graph of $\ln k$ against $\frac{1}{T}$ for the first order decomposition of N_2O_4 into NO_2. Determine the activation energy in kJ mol^{-1} for this reaction. [2]



e.i. Deduce the equilibrium constant expression, K_c, for the reaction. [1]

e.ii. Determine the value of the equilibrium constant, K_c. [3]

e.iii. If the temperature of the reaction is changed to 300 °C, predict, stating a reason in each case, whether the equilibrium concentration of SO_2Cl_2 and the value of K_c will increase or decrease. [3]

e.iv. If the volume of the container is changed to 1.50 dm^3, predict, stating a reason in each case, how this will affect the equilibrium concentration of SO_2Cl_2 and the value of K_c. [3]

e.v. Suggest, stating a reason, how the addition of a catalyst at constant pressure and temperature will affect the equilibrium concentration of SO_2Cl_2. [2]

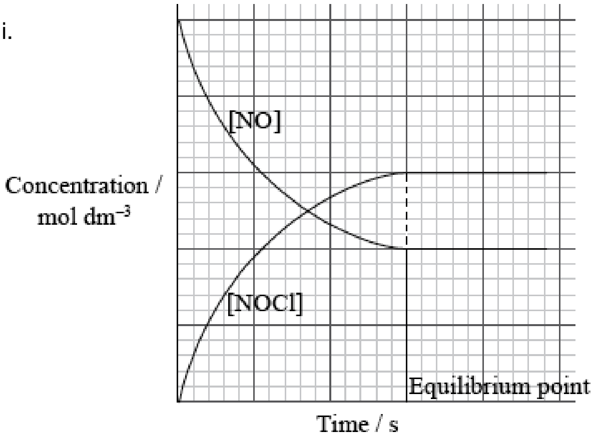
Markscheme

a.i. $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$;

a.ii. rate of reaction will decrease by a factor of 4;

no effect on the rate constant;

a.iii.



y axis labelled concentration/mol dm^{-3} and *x* axis is labelled time/s;

gradient for [NO];

gradient for [NOCl] will be equal and opposite;

equilibrium point identified / two curves level off at same time;

b. Above 775 K: $\text{rate} = k[NO_2][CO]$;

Below 775 K: $\text{rate} = k[NO_2]^2$;

c. zero order reaction;

all concentrations are 1.0 mol dm^{-3};

d. $\text{slope} = \frac{9.2-8.4}{(3.53-3.65)\times10^{-3}} = -6.67 \times 10^3$;

$(E_a = 6.67 \times 10^3 \times 8.31)$

$55.4 \text{ (kJ mol}^{-1}\text{)}$;

Accept in range 55.0 – 56.0

*Award **[1]** if 55454 (J) stated*

*Award **[2]** for the correct final answer*

e.i. $(K_c) = \frac{[SO_2Cl_2]}{[Cl_2][SO_2]}$;

Ignore state symbols.

Square brackets [ ] required for the equilibrium expression.

e.ii. $7.84 \times 10^{-3} \text{ mol of } SO_2$ and $7.84 \times 10^{-3} \text{ mol of } Cl_2$;

$7.84 \times 10^{-3} \text{ mol dm}^{-3} \text{ of } SO_2$, $7.84 \times 10^{-3} \text{ mol dm}^{-3} \text{ of } Cl_2$ **and**
$7.65 \times 10^{-4} \text{ mol dm}^{-3} \text{ of } SO_2Cl_2$;

12.5;

*Award **[1]** for 10.34*

*Award **[3]** for the correct final answer*

e.iii value of K_c increases;

$[SO_2Cl_2]$ increases;

decrease in temperature favours (forward) reaction which is exothermic;

Do not allow ECF.

e.iv no effect on the value of K_c / depends only on temperature;

$[SO_2Cl_2]$ decreases;

increase in volume favours the reverse reaction which has more gaseous moles;

Do not allow ECF.

e.v. no effect;

catalyst increases the rate of forward and reverse reactions (equally) / catalyst decreases activation energies (equally);

Examiners report

a.i. In part (a) the rate expression was correctly stated although some confused this with an equilibrium constant expression.

a.ii.Only the better candidates realized that the rate of reaction will decrease by a factor of four and there will be no effect on the rate constant.

a.iiiAlthough most candidates were able to correctly sketch the concentration versus time graph many forgot to label the axes or include units.

b. Part (b) was well answered and candidates demonstrated a good understanding of rate expressions based on reaction mechanism.

c. The better candidates were able to figure out that the rate of a chemical reaction is equal to the rate constant when all concentrations are $1.0\ \text{mol dm}^{-3}$ or for a zero order reaction.

d. Most candidates had difficulty in calculating activation energy from the graph in part (d) and some gave the answer in J mol^{-1} instead of kJ mol^{-1} which showed that they missed this instruction in the question.

e.i. In part (e), the equilibrium constant expression was correctly stated by the majority but calculating the value ofK_c proved to be difficult.

e.iiA large number of candidates obtained the incorrect answer of 10.34 as a result of using the initial concentrations of the reactants instead of equilibrium concentrations.

e.iii.[N/A]

e.ivThe application of Le Chatelier's principle was handled well by the majority with minor omissions such as not using the term gaseous particles in part (iv).

e.v.Some candidates stated that the addition of a catalyst does not affect the value of K_c or the position of equilibrium, which did not answer the question and scored no marks because they had not commented on the concentration of $SOCl_2$. Some candidates correctly stated that a catalyst increases the rate of forward and reverse reactions equally.

A class studied the equilibrium established when ethanoic acid and ethanol react together in the presence of a strong acid, using propanone as an inert solvent. The equation is given below.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

One group made the following **initial mixture**:

Liquid	**Volume / cm^3**
Ethanoic acid	5.00 ± 0.05
Ethanol	5.00 ± 0.05
$6.00\ \text{mol dm}^{-3}$ aqueous hydrochloric acid	1.00 ± 0.02
Propanone	39.0 ± 0.5

After one week, a $5.00 \pm 0.05\ \text{cm}^3$ sample of the final equilibrium mixture was pipetted out and titrated with $0.200\ \text{mol dm}^{-3}$ aqueous sodium hydroxide to determine the amount of ethanoic acid remaining. The following titration results were obtained:

Titration number	1	2	3
Initial reading / $cm^3 \pm 0.05$	1.20	0.60	14.60
Final reading / $cm^3 \pm 0.05$	28.80	26.50	40.70
Titre / cm^3	27.60	25.90	26.10

a. The density of ethanoic acid is $1.05\ \mathrm{g\,cm^{-3}}$. Determine the amount, in mol, of ethanoic acid present in the initial mixture. [3]

b. The concentration of ethanoic acid can be calculated as $1.748\ \mathrm{mol\,dm^{-3}}$. Determine the percentage uncertainty of this value. (Neglect any uncertainty in the density and the molar mass.) [3]

c.i. Calculate the absolute uncertainty of the titre for Titration 1 ($27.60\ \mathrm{cm^3}$). [1]

c.ii. Suggest the average volume of alkali, required to neutralize the $5.00\ \mathrm{cm^3}$ sample, that the student should use. [1]

c.iii $3.00\ \mathrm{cm^3}$ of the $0.200\ \mathrm{mol\,dm^{-3}}$ aqueous sodium hydroxide reacted with the hydrochloric acid present in the $5.00\ \mathrm{cm^3}$ sample. Determine the concentration of ethanoic acid in the final equilibrium mixture. [2]

c.iv Deduce the equilibrium constant expression for the reaction. [1]

c.v. The other concentrations in the equilibrium mixture were calculated as follows: [1]

Compound	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Concentration / $mol\ dm^{-3}$	0.884	0.828	1.80

Use these data, along with your answer to part (iii), to determine the value of the equilibrium constant. (If you did not obtain an answer to part (iii), assume the concentrations of ethanol and ethanoic acid are equal, although this is not the case.)

d. Outline how you could establish that the system had reached equilibrium at the end of one week. [1]

e. Outline why changing the temperature has only a very small effect on the value of the equilibrium constant for this equilibrium. [1]

f. Outline how adding some ethyl ethanoate to the initial mixture would affect the amount of ethanoic acid converted to product. [2]

g. Propanone is used as the solvent because one compound involved in the equilibrium is insoluble in water. Identify this compound and explain why it is insoluble in water. [2]

h. Suggest **one** other reason why using water as a solvent would make the experiment less successful. [1]

Markscheme

a. $\mathrm{M(CH_3COOH)}\ (= (4 \times 1.01) + (2 \times 12.01) + (2 \times 16.00)) = 60.06\ (\mathrm{g\,mol^{-1}})$;

Accept 60 (g mol⁻¹).

$\text{mass}\ (\mathrm{CH_3COOH})\ (= 5.00 \times 1.05) = 5.25\ (\mathrm{g})$;

$\frac{5.25}{60.06} = 0.0874\ (\mathrm{mol})$;

*Award **[3]** for correct final answer.*

Accept 0.0875 (comes from using Mr = 60 g mol⁻¹).

b. percentage uncertainty in volume of ethanoic acid $= 100 \times \frac{0.05}{5.00} = 1\%$;

percentage uncertainty in total volume $= 100 \times \frac{0.62}{50} = 1.24\%$;

total percentage uncertainty $= 1 + 1.24 = 2.24\%$;

Accept rounding down to 2.2/2%.

c.i. $\pm 0.1/0.10\ (\text{cm}^3)$;

Do ***not*** *accept without ±.*

c.ii. $26.00\ (\text{cm}^3)$;

c.iii. $26.00 - 3.00 = 23.00\ (\text{cm}^3)$;

If other methods used, award ***M1*** *for calculating amount of NaOH reacting with* CH_3COOH*.*

$0.200 \times \frac{23.00}{5.00} = 0.920\ (\text{mol dm}^{-3})$;

Award ***[2]*** *for correct final answer.*

If (ii) given as mean titre (26.5 cm^3*) then ECF answer comes to 0.94 (mol* dm^{-3}*).*

c.iv. $(K_c =)\frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]}$;

Do not penalize minor errors in formulas.

Accept $(K_c =)\frac{[esther][water]}{[ethanol/alcohol][(ethanoic)\ acid]}$.

c.v. $(K_c =)\frac{0.828 \times 1.80}{0.884 \times 0.920} = 1.83$;

If assumed $[CH_3COOH] = 0.884\ \text{mol dm}^{-3}$*, answer is 1.91 – allow this even if an answer was obtained for (iii).*

If (ii) given as mean titre (26.5 cm^3*) then ECF answer comes to 1.79.*

d. repeat the titration a day/week later (and result should be the same) / *OWTTE*;

Accept “concentrations/physical properties/macroscopic properties of the system do not change”.

e. enthalpy change/ΔH for the reaction is (very) small / *OWTTE*;

f. decreases (the amount of ethanoic acid converted);

Accept “increases amount of ethanoic acid present at equilibrium” / OWTTE.

(adding product) shifts position of equilibrium towards reactants/LHS / increases

the rate of the reverse reaction / *OWTTE*;

g. ethyl ethanoate/$CH_3COOC_2H_5$/ester;

forms only weak hydrogen bonds (to water);

Allow “does not hydrogen bond to water” / “hydrocarbon sections too long” / OWTTE.

M2 can only be given only if M1 correct.

h. (large excess of) water will shift the position of equilibrium (far to the left) / *OWTTE*;

Accept any other chemically sound response, such as “dissociation of ethanoic acid would affect equilibrium”.

Examiners report

a. Generally candidates found this question quite challenging and some left quite a number of parts unanswered. The tradition is that the first question on the paper is a data response question, which often addresses many aspects of the syllabus, and unfortunately candidates, especially those of average or below average ability, seem to have difficulty in tackling questions of this nature. One other issue with data response questions is that, of necessity, the data appears at the beginning of the question whilst, mainly because of the space left for candidates to answer, the later parts of the question referring to these data may not appear until a number of pages into the paper.

Part (a) concerning density, volume and amount of substance was generally reasonably well answered, but the following parts, concerning uncertainties, were rarely answered correctly and a number confused precision (uncertainty, either absolute or as a percentage) and accuracy (percentage error in the value obtained). Many candidates also seemed to lack experimental common sense, simply taking an average that included an initial titre that was much larger than the concordant second and third titres, rather than excluding it. This lack of experimental “know how” was also evident in responses to (c) (iii) where it was unusual for the approach to the question to indicate the candidate had realised that the alkali was neutralising two different acids (HCl and $\mathrm{CH_3COOH}$) and again in part (d) where it was rare for the response to outline a practical solution to the problem, though quite a number of candidates suggested that the pH would become constant, presumably not realising that the pH would be dominated by the HCl catalyst. Most students could however carry out the more routine tasks of writing an equilibrium constant expression and determining its value from the data given. Many candidates were aware of Le Chatelier effects on the position of equilibrium, but a significant number failed to use this information to answer the question actually asked and the unusual approach to the effect of temperature disconcerted many. Whilst most students managed to identify the ester as the component of the mixture that was insoluble in water, the reasons given were usually couched in terms of the polarity of the molecule (many quite polar molecules, halogenoalkanes for example, are insoluble in water) rather than its inability to form strong hydrogen bonds to water, which is the critical factor. Quite a number of students came up with a valid reason why water would not be a suitable solvent, though some students appeared to have overlooked the fact the question stated “other reason”.

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A mixture of 1.00 mol SO_2(g), 2.00 mol O_2(g) and 1.00 mol SO_3(g) is placed in a 1.00 dm^3 container and allowed to reach equilibrium.

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

c.i. Nitrogen oxide is in equilibrium with dinitrogen dioxide. [1]

$2NO(g) \rightleftharpoons N_2O_2(g) \quad \Delta H^{\ominus} < 0$

Deduce, giving a reason, the effect of increasing the temperature on the concentration of N_2O_2.

c.ii. A two-step mechanism is proposed for the formation of NO_2(g) from NO(g) that involves an exothermic equilibrium process. [2]

First step: $2NO(g) \rightleftharpoons N_2O_2(g)$ fast

Second step: $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ slow

Deduce the rate expression for the mechanism.

d. The rate constant for a reaction doubles when the temperature is increased from 25.0 °C to 35 °C. [2]

Calculate the activation energy, E_a, in kJ mol^{-1} for the reaction using section 1 and 2 of the data booklet.

Markscheme

c.i. $[N_2O_2]$ decreases ***AND*** exothermic «thus reverse reaction favoured»

Accept "product" for $[N_2O_2]$.

*Do **not** accept just "reverse reaction favoured/shift to left" for "$[N_2O_2]$ decreases".*

[1 mark]

c.ii ***ALTERNATIVE 1:***

«from equilibrium, step 1»

$$K_c = \frac{[N_2O_2]}{[NO]^2}$$

OR

$[N_2O_2] = K_c[NO]^2$

«from step 2, rate «= $k_1[N_2O_2][O_2] = k_2K[NO]^2[O_2]$»

rate = $k[NO]^2[O_2]$

ALTERNATIVE 2:

«from step 2» rate = $k_2[N_2O_2][O_2]$

«from step 1, $\text{rate}_{(1)} = k_1[NO]^2 = k_{-1}[N_2O_2]$, $[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$»

«rate = $\frac{k_1}{k_{-1}} k_2[NO]^2[O_2]$»

rate = $k[NO]^2[O_2]$

*Award **[2]** for correct rate expression.*

[2 marks]

d. «$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$»

T_2 = «273 + 35 =» 308 K ***AND*** T_1 = «273 + 25 =» 298 K

E_a = 52.9 «kJ mol^{-1}»

*Award **[2]** for correct final answer.*

[2 marks]

Examiners report

c.i. [N/A]
c.ii. [N/A]
d. [N/A]

In an experiment conducted at 25.0 °C, the initial concentration of propanoic acid and methanol were $1.6\ \mathrm{mol\,dm^{-3}}$ and $2.0\ \mathrm{mol\,dm^{-3}}$ respectively.

Once equilibrium was established, a sample of the mixture was removed and analysed. It was found to contain $0.80\ \mathrm{mol\,dm^{-3}}$ of compound **X**.

a. Two compounds, **A** and **D**, each have the formula $\mathrm{C_4H_9Cl}$. [5]

Compound **A** is reacted with dilute aqueous sodium hydroxide to produce compound **B** with a formula of $\mathrm{C_4H_{10}O}$. Compound **B** is then oxidized with acidified potassium

manganate(VII) to produce compound **C** with a formula of $\mathrm{C_4H_8O}$. Compound **C** resists further oxidation by acidified potassium manganate(VII).

Compound **D** is reacted with dilute aqueous sodium hydroxide to produce compound **E** with a formula of $\mathrm{C_4H_{10}O}$. Compound **E** does not react with acidified potassium manganate(VII).

Deduce the structural formulas for compounds **A**, **B**, **C**, **D** and **E**.

A:

B:

C:

D:

E:

b. Deduce an equation for the reaction between propanoic acid and methanol. Identify the catalyst and state the name of the organic compound, **X**, formed. [4]

c.i. Calculate the concentrations of the other three species present at equilibrium. [3]

c.ii. State the equilibrium constant expression, K_c, and calculate the equilibrium constant for this reaction at 25.0 °C. [2]

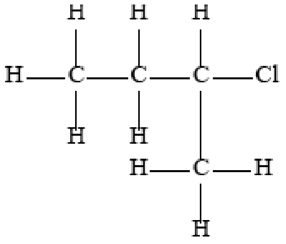
d.i. 2-chloro-3-methylbutane reacts with sodium hydroxide via an $\mathrm{S_N2}$ mechanism. Explain the mechanism by using curly arrows to represent the movement of electron pairs. [4]

d.ii. Explain why the hydroxide ion is a better nucleophile than water. [2]

d.iii. 1-chlorobutane can be converted to a pentylamine via a two stage process. Deduce equations for each step of this conversion including any catalyst required **and** name the organic product produced at **each** stage. [5]

Markscheme

a. **A**:



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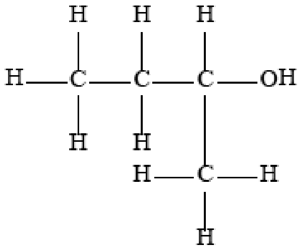
B:



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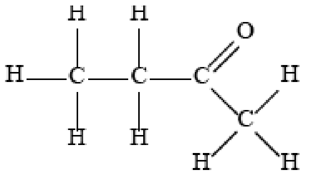
C:



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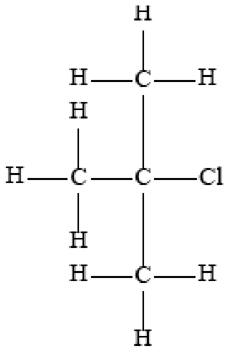
D:



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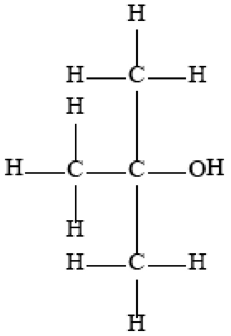
E:



;

Accept condensed formulas.

*Award **[1 max]** if **A** and **D** are other way round (and nothing else correct).*

*Award **[2 max]** if **A** and **D** are other way round but one substitution product **B** or **E** is correct based on initial choice of **A** and **D**.*

*Award **[3 max]** if **A** and **D** are other way round but both substitution products **B** and **E** are correct based on initial choice of **A** and **D**.*

*M2 (for **B**) and M5 (for **E**) may also be scored for substitution product if primary chloroalkane used.*

Penalize missing hydrogens once only in Q.7.

b.

$$\mathrm{CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O}$$

***[1]** for reactants and **[1]** for products.*

(concentrated) sulfuric acid/$\mathrm{H_2SO_4}$;

Do not accept just H^+ or acid.

methyl propanoate;

c.i. *[CH$_3$CH$_2$COOH]:*

$(1.6 - 0.80 =)\ 0.8\ (\mathrm{mol\,dm^{-3}})$;

[CH$_3$OH]:

$(2.0 - 0.80 =)\ 1.2\ (\mathrm{mol\,dm^{-3}})$;

[H$_2$O]:

$0.80\ (\mathrm{mol\,dm^{-3}})$;

c.ii. $(K_\mathrm{c} =)\frac{[\mathrm{CH_3CH_2COOCH_3}][\mathrm{H_2O}]}{[\mathrm{CH_3CH_2COOH}][\mathrm{CH_3OH}]}$;

$\left(K_c = \frac{[(0.80)^2]}{[(1.2\times 0.8)]} = \right)$ 0.7;

Allow 0.67.

*Award **[1 max]** for 0.83.*

d.i. curly arrow going from lone pair/negative charge on O in HO^- to C;

Do not allow curly arrow originating on H in HO^-.

curly arrow showing Cl leaving;

Accept curly arrow either going from bond between C and Cl to Cl in 2-chloro-3-methylbutane or in the transition state.

representation of transition state showing negative charge, square brackets and partial bonds;

Do not penalize if HO and Cl are not at 180° to each other.

Do not award M3 if OH ---- C bond is represented.

formation of organic product 3-methylbutan-2-ol **and** Cl^-;

d.ii. OH^- has a negative charge/higher electron density;

greater attraction to the carbon atom (with the partial positive charge) / *OWTTE*;

Do not allow just greater attraction.

d.iii. $CH_3CH_2CH_2CH_2Cl + KCN \rightarrow CH_3CH_2CH_2CH_2CN + KCl$;

Accept CN^- for KCN and Cl^- for KCl.

pentanenitrile;

Allow 1-cyanobutane.

$CH_3CH_2CH_2CH_2CN + 2H_2 \rightarrow CH_3CH_2CH_2CH_2CH_2NH_2$;

pentan-1-amine / 1-aminopentane / 1-pentylamine / 1-pentanamine;

Catalyst: nickel/Ni / palladium/Pd / platinum/Pt;

Penalise missing hydrogen once only in Q.7.

Examiners report

a. This was the least popular question in Section B. Most candidates either scored all five marks in (a) or just one.

b. (b) was usually well done, though it was disappointing that more candidates did not use the equilibrium sign.

c.i. In (c), a significant number of candidates omitted water from the equilibrium calculations.

c.ii. In (c), a significant number of candidates omitted water from the equilibrium calculations.

d.i. The organic reaction mechanism in (d) (i) was very poorly presented. Many even tried drawing curly arrows from NaOH as an attacking species. The majority could identify the product of the reaction but a mechanism was far beyond them. Transition states were poor or missing completely.

d.ii. In (ii) although many knew that OH^- has a negative charge, few linked this to the greater attraction to the carbon atom.

d.iii. In (iii) very few candidates did well here and the name of pentan-1-amine was rarely given. Other mistakes included incorrect catalysts. Further common mistakes included some candidates not including all the hydrogens in the structural formulas. In general for this part there was very poor knowledge of organic synthesis amongst candidates. Very few had a good “stab” at this question. The fact that pentylamine was mentioned in the question initially meant that very few candidates accessed the last mark for the name of the product.

Bonds can be formed in many ways.

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The equilibrium for a mixture of NO_2 and N_2O_4 gases is represented as:

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

At 100°C, the equilibrium constant, K_c, is 0.21.

b.i. Discuss the bonding in the resonance structures of ozone. [3]

b.ii Deduce one resonance structure of ozone and the corresponding formal charges on each oxygen atom. [2]

c. The first six ionization energies, in kJ mol^{-1}, of an element are given below. [2]

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
578	1816	2744	11576	14829	18375

Explain the large increase in ionization energy from IE_3 to IE_4.

d.i. At a given time, the concentration of NO_2(g) and N_2O_4(g) were 0.52 and 0.10 mol dm^{-3} respectively. [2]

Deduce, showing your reasoning, if the forward or the reverse reaction is favoured at this time.

d.ii Comment on the value of ΔG when the reaction quotient equals the equilibrium constant, $Q = K$. [2]

Markscheme

b.i. lone pair on p orbital «of O atom» overlaps/delocalizes with pi electrons «from double bond»

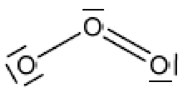
both O–O bonds have equal bond length
OR
both O–O bonds have same/1.5 bond order
OR
both O–O are intermediate between O–O ***AND*** O=O

both O–O bonds have equal bond energy

Accept "p/pi/π electrons are delocalized/not localized".

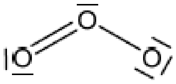
[3 marks]

b.ii ***ALTERNATIVE 1:***



FC: –1 ***AND*** +1 ***AND*** 0

ALTERNATIVE 2:



FC: 0 ***AND*** +1 ***AND*** –1

Accept any combination of lines, dots or crosses to represent electrons.

Do not accept structure that represents 1.5 bonds.

Do not penalize missing lone pairs if already penalized in 3(b).

If resonance structure is incorrect, no ECF.

Any one of the structures with correct formal charges for ***[2 max]****.*

[2 marks]

c. *Any two of:*

IE_4: electron in lower/inner shell/energy level

OR

IE_4: more stable/full electron shell

IE_4: electron closer to nucleus
OR
IE_4: electron more tightly held by nucleus

IE_4: less shielding by complete inner shells

Accept "increase in effective nuclear charge" for M2.

[2 marks]

d.i. «$Q_c = \frac{0.10}{0.52^2}$ =» 0.37

reaction proceeds to the left/NO_2(g) «until $Q = K_c$»

OR

reverse reaction «favoured»

Do not award M2 without a calculation for M1 but remember to apply ECF.

[2 marks]

d.ii $\Delta G = 0$

reaction at equilibrium

OR

rate of forward and reverse reaction is the same

OR

constant macroscopic properties

[2 marks]

Examiners report

b.i. [N/A]
b.ii. [N/A]
c. [N/A]
d.i. [N/A]
d.ii. [N/A]

Many reactions are in a state of equilibrium.

The following reaction was allowed to reach equilibrium at 761 K.

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g) \qquad \Delta H^{\theta} < 0$$

The pH of 0.010 mol dm^{-3} carbonic acid, H_2CO_3 (aq), is 4.17 at 25 °C.

$$H_2CO_3\ (aq) + H_2O\ (l) \rightleftharpoons HCO_3^-\ (aq) + H_3O^+\ (aq).$$

a.i. State the equilibrium constant expression, K_c , for this reaction. [1]

a.ii. The following equilibrium concentrations in mol dm^{-3} were obtained at 761 K. [1]

$[H_2(g)]$	$[I_2(g)]$	$[HI\,(g)]$
8.72×10^{-4}	2.72×10^{-3}	1.04×10^{-2}

Calculate the value of the equilibrium constant at 761 K.

a.iii Determine the value of ΔG^{θ}, in kJ, for the above reaction at 761 K using section 1 of the data booklet. [1]

c.i. Calculate $[H_3O^+]$ in the solution and the dissociation constant, K_a , of the acid at 25 °C. [3]

c.ii. Calculate K_b for HCO_3^- acting as a base. [1]

Markscheme

a.i. $K_c = \frac{[HI]^2}{[H_2][I_2]}$

a.ii. 45.6

a.iii ΔG^{θ} = «$-RT \ln K$ = – (0.00831 kJ K^{-1} mol^{-1} x 761 K x ln 45.6) =» – 24.2 «kJ»

c.i. $[H_3O^+] = 6.76 \times 10^{-5}$ «mol dm^{-3}»

$$K_a = \frac{(6.76\times10^{-5})^2}{(0.010-6.76\times10^{-5})} / \frac{(6.76\times10^{-5})^2}{0.010}$$

4.6×10^{-7}

Accept 4.57×10^{-7}

*Award **[3]** for correct final answer.*

c.ii.« $\frac{1.00\times10^{-14}}{4.6\times10^{-7}}$ =» 2.17 x 10^{-8}

OR

« $\frac{1.00\times10^{-14}}{4.57\times10^{-7}}$ =» 2.19 x 10^{-8}

Examiners report

a.i. [N/A]
a.ii. [N/A]
a.iii. [N/A]
c.i. [N/A]
c.ii. [N/A]

When nitrogen gas and hydrogen gas are allowed to react in a closed container the following equilibrium is established.

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}\ \Delta H = -92.6\ \mathrm{kJ}$$

a.i. Outline **two** characteristics of a reversible reaction in a state of dynamic equilibrium. [2]

a.ii. Predict, with a reason, how each of the following changes affects the position of equilibrium. [2]

The volume of the container is increased.

Ammonia is removed from the equilibrium mixture.

a.iii. Define the term *activation energy*, E_a. [1]

b. Ammonia is manufactured by the Haber process in which iron is used as a catalyst. [2]

Explain the effect of a catalyst on the rate of reaction.

c. Typical conditions used in the Haber process are 500 °C and 200 atm, resulting in approximately 15% yield of ammonia. [3]

(i) Explain why a temperature lower than 500 °C is **not** used.

(ii) Outline why a pressure higher than 200 atm is **not** often used.

d.i. Deduce the equilibrium constant expression, K_c, for the reaction on page 10. [1]

d.ii. When 1.00 mol of nitrogen and 3.00 mol of hydrogen were allowed to reach equilibrium in a $1.00\ \mathrm{dm^3}$ container at a temperature of 500 °C and a pressure of 1000 atm, the equilibrium mixture contained 1.46 mol of ammonia. [2]

Calculate the value of K_c at 500 °C.

e.i. Define the term *base* according to the Lewis theory. [1]

e.ii.Define the term *weak base* according to the Brønsted–Lowry theory. [1]

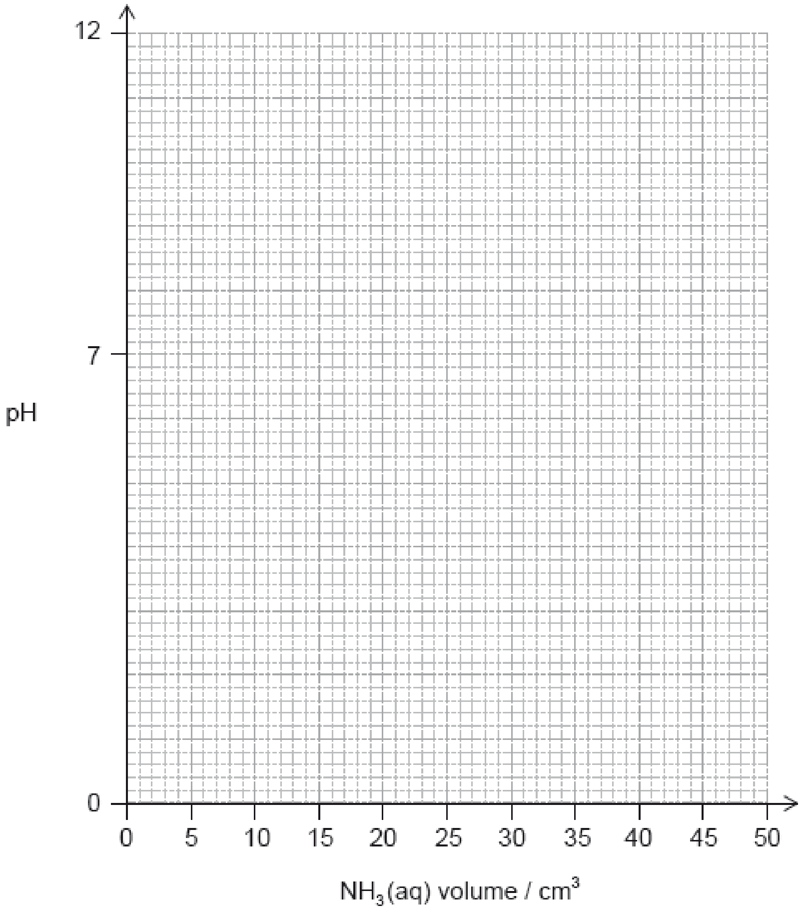
e.iiiDeduce the formulas of conjugate acid-base pairs in the reaction below. [2]

$$\mathrm{CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)}$$

Acid	**Conjugate base**
. . . .	. . . .
. . . .	. . . .

f. Determine the pH of a $0.100\ \mathrm{mol\,dm^{-3}}$ solution of ammonia, $\mathrm{NH_3(aq)}$, using tables 2 and 15 of the data booklet. [4]

g. (i) Sketch the pH titration curve obtained when $50.0\ \mathrm{cm^3}$ of $0.100\ \mathrm{mol\,dm^{-3}NH_3(aq)}$ is added to $25.0\ \mathrm{cm^3}$ of $0.100\ \mathrm{mol\,dm^{-3}HCl\ (aq)}$. [4]



(ii) Identify an indicator from table 16 of the data booklet that could be used for this titration.

Markscheme

a.i. rates of forward **and** reverse reactions are equal / opposing changes occur at equal rates;

the concentrations of all reactants **and** products remain constant / macroscopic properties remain constant;

closed/isolated system;

Accept "the same" for "equal" in M1 and for "constant" in M2.

a.ii.*The volume of the container is increased:*

position of equilibrium shifts to the left/reactants **and** fewer moles of gas on the right hand side/pressure decreases / *OWTTE*;

Ammonia is removed from the equilibrium mixture:

position of equilibrium shifts to the right/products **and** $[\mathrm{NH_3}]$ decreases so $[\mathrm{N_2}]$ and $[\mathrm{H_2}]$ must also decrease to keep K_c constant

OR

position of equilibrium shifts to the right/products **and** rate of reverse reaction decreases / *OWTTE*;

*Award **[1 max]** if both predicted changes are correct.*

Do not accept "to increase $[NH_3]$" or reference to LCP without explanation.

a.iii. minimum energy needed (by reactants/colliding particles) to react/start/initiate a reaction;

Accept "energy difference between reactants and transition state".

b. more effective/successful collisions per unit time / greater proportion of collisions effective;

alternative pathway **and** a lower activation energy

OR

lowers activation energy so that more particles have enough energy to react;

Do not accept just "lowers/reduces the activation energy".

Accept "provides a surface for reacting/reactants/reaction".

c. (i) slower rate / *OWTTE*;

uneconomic / *OWTTE*;

(ii) high cost for building/maintaining plant / high energy cost of compressor / *OWTTE*;

Do not accept "high pressure is expensive" without justification.

Accept high pressure requires high energy.

d.i. $(K_c =)\frac{[\mathrm{NH_3(g)}]^2}{[\mathrm{N_2(g)}]\times[\mathrm{H_2(g)}]^3}$;

Ignore state symbols.

Concentrations must be represented by square brackets.

d.ii. moles at equilibrium: nitrogen 0.27, hydrogen 0.81 / concentrations at equilibrium: nitrogen $0.27\ (\mathrm{mol\,dm^{-3}})$, hydrogen $0.81\ (\mathrm{mol\,dm^{-3}})$ (and ammonia $1.46\ \mathrm{mol\,dm^{-3}}$);

$K_c = 15$;

Actual calculation gives $K_c = 14.86$.

*Award **[2]** for correct final answer.*

*Award **[1 max]** if $K_c\left(=\frac{1.46^2}{3^3\times1}\right) = 0.079$*

e.i. electron pair donor;

Accept lone pair donor.

e.ii. proton acceptor **and** partially/slightly ionized;

*Accept "proton acceptor **and** partially/slightly dissociated".*

e.iii.

Acid		Conjugate base
$CH_3NH_3^+$	**and**	CH_3NH_2;
H_2O	**and**	OH^-;

*Award **[1 max]** for two correct acids OR two correct conjugate bases.*

f. $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}/10^{-4.75}$;

$[NH_4^+] = [OH^-]$ **and** $[NH_3] \approx 1.00 \times 10^{-1}$ (mol dm^{-3});

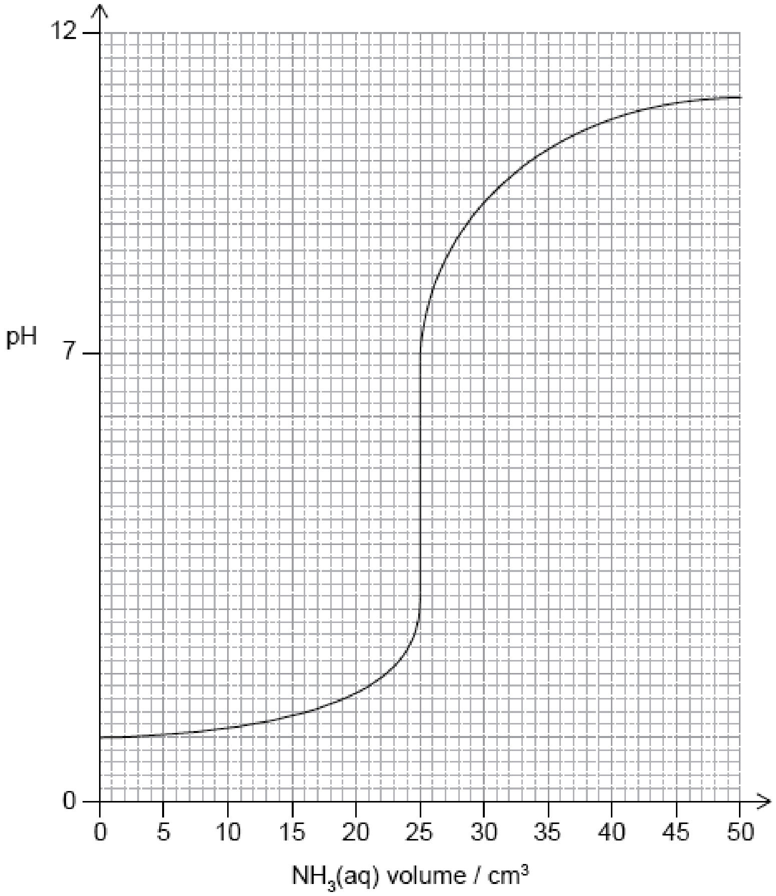
$[OH^-] = (\sqrt{1.8 \times 10^{-6}} =)1.3 \times 10^{-3}$ $(\text{mol dm}^{-3})/\text{pOH} = 2.89$;

$\text{pH} = (14.0 - 2.89 =)11.1$;

*Award **[4]** for correct final answer.*

g.

(i)



For volume $= 0$: $\text{pH} = 1$;

<u>vertical</u> jump should be positioned in volume range $24\ \text{cm}^3$ to $26\ \text{cm}^3$ and include pH range between 3 to 6;

For volume = 50: pH between 8 to 11;

(ii) methyl orange / bromophenol blue / bromocresol green / methyl red;

Examiners report

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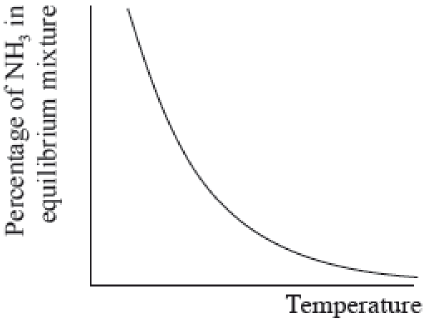
The Haber process enables the large-scale production of ammonia needed to make fertilizers.

The equation for the Haber process is given below.

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

The percentage of ammonia in the equilibrium mixture varies with temperature.



Ammonia can be converted into nitric acid, $HNO_3(aq)$, and hydrocyanic acid, HCN(aq). The pK_a of hydrocyanic acid is 9.21.

A student decided to investigate the reactions of the two acids with separate samples of 0.20 mol dm^{-3} sodium hydroxide solution.

a. (i) Use the graph to deduce whether the forward reaction is exothermic or endothermic and explain your choice. [9]

(ii) State and explain the effect of increasing the pressure on the yield of ammonia.

(iii) Deduce the equilibrium constant expression, K_c, for the reaction.

(iv) A mixture of 1.00 mol N_2 and 3.00 mol H_2 was placed in a 1.0 dm^3 flask at 400 °C. When the system was allowed to reach equilibrium, the concentration of was found to be $0.062 \text{ mol dm}^{-3}$. Determine the equilibrium constant, K_c, of the reaction at this temperature.

(v) Iron is used as a catalyst in the Haber process. State the effect of a catalyst on the value of K_c.

b. (i) Distinguish between the terms *strong* and *weak acid* and state the equations used to show the dissociation of each acid in aqueous solution. [9]

(ii) Deduce the expression for the ionization constant, K_a, of hydrocyanic acid and calculate its value from the pK_a value given.

(iii) Use your answer from part (b) (ii) to calculate the $[H^+]$ and the pH of an aqueous solution of hydrocyanic acid of concentration $0.108 \text{ mol dm}^{-3}$. State **one** assumption made in arriving at your answer.

c. A small piece of magnesium ribbon is added to solutions of nitric and hydrocyanic acid of the same concentration at the same temperature. [2]

Describe **two** observations that would allow you to distinguish between the two acids.

d. (i) Calculate the volume of the sodium hydroxide solution required to react exactly with a 15.0 cm^3 solution of 0.10 mol dm^{-3} nitric acid. [3]

(ii) The following hypothesis was suggested by the student: "Since hydrocyanic acid is a weak acid it will react with a smaller volume of the 0.20 mol dm^{-3} sodium hydroxide solution." Comment on whether or not this is a valid hypothesis.

(iii) Use Table 16 of the Data Booklet to identify a suitable indicator for the titration of sodium hydroxide and hydrocyanic acid.

Markscheme

a. (i) exothermic;

Accept either of the following for the second mark.

increasing temperature favours endothermic/reverse reaction;

as yield decreases with increasing temperature;

(ii) yield increases / equilibrium moves to the right / more ammonia;

increase in pressure favours the reaction which has fewer moles of gaseous products;

(iii) $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$;

(iv) $[N_2]$: (at equilibrium $= 1.00 - 0.031 =$) $0.969 \text{ (mol dm}^{-3})$;

$[H_2]$: (at equilibrium $= 3.00 - 3(0.031) =$) $2.91 \text{ (mol dm}^{-3})$;

$K_c \left(= \frac{(0.062)^2}{(0.969)\,(2.91)^3}\right) = 1.6(1) \times 10^{-4}$;

Ignore units.

Award ***[1]*** *for $K_c = 1.4 \times 10^{-4}$*

(v) no effect;

b. (i) strong acid completely dissociated/ionized **and** weak acid partially dissociated/ionized;

$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$;

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$;

Insist on both arrows as shown.

State symbols not needed.

Accept H_2O and H_3O^+.

(ii) $K_a = \frac{[H^+][CN^-]}{[HCN]}$;

Allow H_3O^+ instead of H^+.

$K_a = 10^{-9.21} = 6.17 \times 10^{-10}$;

(iii) $[H^+] = \sqrt{K_a[HCN]}/\sqrt{(6.17 \times 10^{-10} \times 0.108)}$;

$= 8.16 \times 10^{-6}$;

Allow in the range 8.13 × 10^{-6} to 8.16 × 10^{-6}.

$\text{pH} = 5.09$;

OR

$\text{pH} = \frac{1}{2}(\text{p}K_a - \log[\text{HCN}]) / \frac{1}{2}(9.21 - \log 0.108)$;

$= 5.09$;

$[\text{H}^+] = 10^{-5.09} = 8.16 \times 10^{-6}$;

Allow in the range 8.13 × 10^{-6} to 8.16 × 10^{-6}.

If expression for [H^+] missing but both answers correct, award ***[3]****, if one answer correct, award* ***[2]****.*

assume $[\text{H}^+] \ll 0.108$ / negligible dissociation;

c. *With HNO_3*:

faster rate of bubble/hydrogen/gas production;

faster rate of magnesium dissolving;

higher temperature change;

Accept opposite argument for HCN.

Reference to specific observations needed.

Award ***[1]*** *if 2 observations given but acid is not identified.*

d. (i) (nitric acid) 7.5 cm^3;

(ii) not valid as hydrocyanic acid reacts with same volume/ 7.5 cm^3;

(iii) bromothymol blue / phenol red / phenolphthalein;

Examiners report

a. Equilibrium is a topic that has shown substantial improvement in recent sessions with some very well produced arguments. The reaction was correctly described as exothermic with a reason correctly given in most cases. Most candidates knew that yield would increase with increased pressure, but some failed to identify the change in the number of “gaseous” molecules as the reason. More candidates had difficulty with the equilibrium constant calculation often using the initial not equilibrium concentrations.

b. In (b) most correctly defined strong and weak acids and many also wrote correct equations. A few, however, missed the equilibrium sign for hydrocyanic acid. HA, CH_3COOH and HCl were commonly given instead of HCN and HNO_3, suggesting that students sometimes have difficulty applying general concepts to specific cases. It was encouraging to see many candidates determine the pH from the pK_a value including the assumption that there is negligible dissociation, as this has challenged students in previous sessions. A significant number of weaker candidates reported however that the acid solution would have pH values above 7.

c. Part (c) presented problems with many candidates unable to describe specific observations related to rate which would distinguish between a strong and weak acid and simply stated that the reaction would be faster.

d. The moles calculation was answered well in (d) with most candidates able to identify phenolphthalein as a suitable indicator.

An equilibrium exists between nitrosyl chloride, NOCl, nitrogen oxide, NO, and chlorine, Cl_2.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$20.0\ cm^3$ of hexane, C_6H_{14}, and $20.0\ cm^3$ of pentan-1-ol, $C_5H_{11}OH$, were placed separately into two closed containers at 298 K and allowed to reach equilibrium.

Ammonia is a weak base.

a. (i) Deduce the equilibrium constant expression for this reaction. [7]

(ii) Explain the effect on the position of equilibrium and the value of K_c when pressure is decreased and temperature is kept constant.

(iii) 2.00 mol of NOCl was placed in a $1.00\ dm^3$ container and allowed to reach equilibrium at 298 K. At equilibrium, 0.200 mol of NO was present. Determine the equilibrium concentrations of NOCl and Cl_2, and hence calculate the value of K_c at this temperature.

(iv) The value of K_c is 1.60×10^{-5} at 318 K. State and explain whether the forward reaction is exothermic or endothermic.

b. (i) Compare the two liquids in terms of their boiling points, enthalpies of vaporization and vapour pressures. [4]

(ii) Explain your answer given for part (b)(i).

c.i. Calculate the pH of a $1.50\ mol\ dm^{-3}$ solution of ammonia at 298 K to two decimal places, using Table 15 of the Data Booklet. [2]

c.ii. A buffer solution is made using $25.0\ cm^3$ of $0.500\ mol\ dm^{-3}$ hydrochloric acid, HCl (aq), and $20.0\ cm^3$ of $1.50\ mol\ dm^{-3}$ ammonia solution, $NH_3(aq)$. [2]

Describe the meaning of the term *buffer solution*.

c.iii. Determine the pH of the buffer solution at 298 K. [4]

c.iv.A $1.50\ \text{mol dm}^{-3}$ solution of ammonia is added to $25.0\ \text{cm}^3$ of a $0.500\ \text{mol dm}^{-3}$ hydrochloric acid solution in a titration experiment. [1]

Calculate the total volume of the solution at the equivalence point.

c.v.Calculate the pH of the solution at the equivalence point, using Table 15 of the Data Booklet. [4]

c.vi.Identify a suitable indicator for this titration, using Table 16 of the Data Booklet. [1]

Markscheme

a. (i) $(K_c =)\frac{[Cl_2(g)][NO(g)]^2}{[NOCl(g)]^2}$;

Ignore state symbols.

(ii) equilibrium shifts to right as there are more moles (of gas) on product side;

no change to K_c as it is a constant at fixed temperature / *OWTTE*;

(iii) $[NOCl(g)] = 1.80\ (\text{mol dm}^{-3})$;

$[Cl_2(g)] = 0.100\ (\text{mol dm}^{-3})$;

$K_c = \left(\frac{0.100 \times (0.200)^2}{(1.80)^2}\right) 1.23 \times 10^{-3}\ (\text{mol dm}^{-3})$;

*Award **[3]** for correct final answer.*

(iv) exothermic as K_c is lower at higher temperature;

b. (i) hexane has lower boiling point **and** enthalpy of vaporization than pentan-1-ol / *OWTTE*;

hexane has higher vapour pressure than pentan-1-ol / *OWTTE*;

(ii) hexane is non-polar / has only van der Waals'/London/dispersion forces / has weaker intermolecular forces than pentan-1-ol;

pentan-1-ol has hydrogen bonding between molecules;

c.i. $[OH^-] = \sqrt{1.50 \times 1.78 \times 10^{-5}} = 5.17 \times 10^{-3}\ (\text{mol dm}^{-3})$;

$\text{pH} = (14 - \text{pOH} = 14 - 2.29 =)\ 11.71$;

*Award **[2]** for correct final answer.*

Accept correct answer with more than 2 decimal places.

c.ii.solution which resists change in pH / changes pH slightly / *OWTTE*;

when <u>small</u> amounts of acid or base are added;

c.iii.$[NH_3] = \left(\frac{(1.50 \times 0.0200) - (0.500 \times 0.0250)}{0.0450} =\right)\ 0.389\ (\text{mol dm}^{-3})$;

$[NH_4^+] = \left(\frac{(0.500 \times 0.0250)}{0.0450} =\right)\ 0.278\ (\text{mol dm}^{-3})$;

$[OH^-] = \left(\frac{K_b[NH_3]}{[NH_4^+]} =\right)\ \frac{1.78 \times 10^{-5} \times 0.389}{0.278} = 2.49 \times 10^{-5}\ (\text{mol dm}^{-3})$;

$\text{pH} = (14.0 - \text{pOH} = 14.0 - 4.60 =)\ 9.40$;

OR

$\text{pOH} = \text{p}K_b + \log\frac{[NH_4^+]}{[NH_3]} = \text{p}K_b + \log\frac{(12.5/1000)}{(17.5/1000)}$;

$\text{pOH} = 4.75 + \log\left(\frac{12.5}{17.5}\right) = 4.75 - 0.146 = 4.604$;

$\text{pH} = 14.0 - 4.604 = 9.40$;

*Award **[4]** for the correct final answer.*

c.iv.$\left(\mathrm{V(NH_3)} = \frac{25.0\times0.500}{1.50} = 8.33\ \mathrm{cm^3}\right)$

$\mathrm{V} = \mathrm{V(NH_3)} + \mathrm{V(HCl)} = 8.33 + 25.0 = 33.3\ \mathrm{cm^3}/0.0333\ \mathrm{dm^3}$;

c.v.($\mathrm{NH_4^+}$ ions are present at equivalence point $\mathrm{NH_3 + HCl \rightarrow NH_4^+ + Cl^-}$ at equivalence $\mathrm{n(NH_4^+\ produced) = n(NH_3\ added) = n(HCl)}$)

$[\mathrm{NH_4^+}] = \frac{0.500\times0.0250}{0.0333} = 0.375\ (\mathrm{mol\,dm^{-3}})$;

$(\mathrm{NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)/NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)}$

$\mathrm{p}K_\mathrm{a}(\mathrm{NH_4^+}) = 14 - \mathrm{p}K_\mathrm{b}(\mathrm{NH_3}) = 14.00 - 4.75 = 9.25)$

$K_\mathrm{a} = \frac{[\mathrm{NH_3(aq)}][\mathrm{H^+(aq)}]}{[\mathrm{NH_4^+(aq)}]} = 5.62\times10^{-10}$;

$[\mathrm{H^+(aq)}] = \sqrt{5.62\times10^{-10}\times0.375} = 1.45\times10^{-5}\ (\mathrm{mol\,dm^{-3}})$;

$\mathrm{pH} = 4.84$;

*Award **[4]** for the correct final answer.*

c.vi.bromocresol green / methyl red;

ECF for answer in 7(c)(v) if pH given is below 7.

Examiners report

a. The construction and use of equilibrium expressions for K_c showed good understanding. The prediction of the effect of increasing pressure on the position of equilibria by applying Le Chatelier’s principle was good, but the fact that K_c remains constant at fixed temperatures was less well known.

pH calculations in c(i), c(ii) and c(v) tended to be very good or completely incorrect.

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The rate of reaction is an important factor in industrial processes such as the Contact process to make sulfur trioxide, $SO_3(g)$.

a. Define the term *rate of reaction*. [1]

b. Describe the collision theory. [3]

c.i. The Contact process involves this homogeneous equilibrium: [2]

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198\ kJ$$

State and explain how increasing the pressure of the reaction mixture affects the yield of SO_3.

c.ii.The Contact process involves this homogeneous equilibrium: [4]

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198\ kJ$$

2.00 mol of $SO_2(g)$ are mixed with 3.00 mol of $O_2(g)$ in a $1.00\ dm^3$ container until equilibrium is reached. At equilibrium there are 0.80 mol of $SO_3(g)$.

Determine the equilibrium constant (K_c) assuming all gases are at the same temperature and pressure.

c.iii.The Contact process involves this homogeneous equilibrium: [1]

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198\ kJ$$

State the effect of increasing temperature on the value of K_c for this reaction.

d. Outline the economic importance of using a catalyst in the Contact process. [2]

Markscheme

a. change in concentration of reactant/product with time / rate of change of concentration;

Accept "increase" instead of "change" for product and "decrease" instead of "change" for reactant.

Accept "mass/amount/volume" instead of "concentration".

Do not accept substance.

b. collision frequency;

two particles must collide;

particles must have sufficient energy to overcome the activation energy/$E \geqslant E_a$;

Concept of activation energy must be mentioned.

appropriate collision geometry/orientation;

c.i. increases yield;

(equilibrium shifts to the right/products as) more gaseous moles in reactants/on left / fewer gaseous moles in products/on right;

c.ii. $\text{Eqm}[\text{O}_2] = 2.6\ (\text{mol}\,\text{dm}^{-3})$;

$\text{Eqm}[\text{SO}_2] = 1.2\ (\text{mol}\,\text{dm}^{-3})$;

$K_\text{c} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$;

$K_\text{c} = 0.17$;

*Award **[4]** for correct final answer.*

Ignore units.

c.iii. (K_c) decreases;

d. catalyst increases rate of reaction / equilibrium reached faster / increases yield of product per unit time;

reduces costs / reduces energy needed;

Do not accept just "increases the yield".

Examiners report

a. The definitions of rate of reaction in (a) were poor with many referring to a measure of time rather than a change in concentration. The collision theory was described successfully for the most part with "frequency of collisions" less frequently mentioned. In (c) (i) most realized that the number of moles of gases is important and thus gave a correct answer. Whilst the K_c expression was often given correctly in (ii), the calculation of equilibrium mole concentrations was more testing, particularly that for $[\text{O}_2]$. Many were able to answer (iii) correctly. In part (d) many suggested that it is good to make more of something rather than relating this to a reduction in costs.

b. The definitions of rate of reaction in (a) were poor with many referring to a measure of time rather than a change in concentration. The collision theory was described successfully for the most part with "frequency of collisions" less frequently mentioned. In (c) (i) most realized that the number of moles of gases is important and thus gave a correct answer. Whilst the K_c expression was often given correctly in (ii), the calculation of equilibrium mole concentrations was more testing, particularly that for $[\text{O}_2]$. Many were able to answer (iii) correctly. In part (d) many suggested that it is good to make more of something rather than relating this to a reduction in costs.

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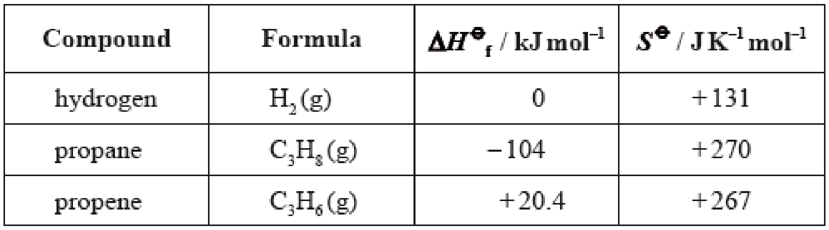
An example of a homogeneous reversible reaction is the reaction between hydrogen and iodine.

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

Propene can be hydrogenated in the presence of a nickel catalyst to form propane. Use the data below to answer the questions that follow.



Compound	Formula	$\Delta H^{\ominus}_{f}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
hydrogen	$H_2(g)$	0	+131
propane	$C_3H_8(g)$	−104	+270
propene	$C_3H_6(g)$	+20.4	+267

a.v.At a temperature just above 700 K it is found that when 1.60 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium in a $4.00\ \mathrm{dm}^3$ flask, the amount of hydrogen iodide formed in the equilibrium mixture is 1.80 mol. Determine the value of the equilibrium constant at this temperature. [4]

b.i.Outline why the value for the standard enthalpy change of formation of hydrogen is zero. [1]

b.ii.Calculate the standard enthalpy change for the hydrogenation of propene. [2]

b.iii.Calculate the standard entropy change for the hydrogenation of propene. [2]

b.iv.Determine the value of ΔG^{Θ} for the hydrogenation of propene at 298 K. [2]

b.v.At 298 K the hydrogenation of propene is a spontaneous process. Determine the temperature above which propane will spontaneously decompose into propene and hydrogen. [2]

Markscheme

a.v.amount of $\mathrm{H_2}$ remaining at equilibrium $= 1.60 - \frac{1.80}{2} = 0.70\ \mathrm{mol}$;

amount of $\mathrm{I_2}$ remaining at equilibrium $= 1.0 - \frac{1.80}{2} = 0.10\ \mathrm{mol}$;

$K_\mathrm{c} = \frac{(1.80/4.0)^2}{(0.70/4.00)\times(0.10/4.00)} \Big/ \frac{1.80^2}{0.70\times0.10}$;

$K_\mathrm{c} = \frac{(1.80)^2}{0.70\times0.10} = 46.3$;

*Award **[4]** for correct final answer.*

b.i.by definition $\Delta H_\mathrm{f}^{\Theta}$ of elements (in their standard states) is zero / no reaction involved / *OWTTE*;

b.ii.$\Delta H = -104 - (+20.4)$;

$= -124.4\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[1 max]** for 124.4 (kJ mol^{-1}).*

*Award **[2]** for correct final answer.*

b.iii.$\Delta S = 270 - (267 + 131)$;

$= -128\ (\mathrm{J\,K^{-1}mol^{-1}})$;

*Award **[1 max]** for +128 (J K^{-1}mol^{-1}).*

*Award **[2]** for correct final answer.*

b.iv.$\Delta G = \Delta H - \mathrm{T}\Delta S = -124.4 - \frac{(-128\times298)}{1000}$;

$= -86.3\ \mathrm{kJ\,mol^{-1}}$;

Units needed for the mark.

*Award **[2]** for correct final answer.*

Allow ECF if only one error in first marking point.

b.v.$\Delta G = \Delta H - \mathrm{T}\Delta S = 0 / \Delta H = \mathrm{T}\Delta S$;

$\mathrm{T} = \frac{-124.4}{-128/1000} = 972\ \mathrm{K}/699\ ^\circ\mathrm{C}$;

Only penalize incorrect units for T and inconsistent ΔS value once in (iv) and (v).

Examiners report

a.v.This was the most popularly answered question. Most candidates were able to give a good description of the characteristics of homogenous equilibrium, and apply Le Chatelier‟s Principle to explain the effect of catalysts and changes of temperature and pressure on the position of equilibrium and the equilibrium constant. A good majority were able to calculate the value of K_c although a significant number of candidates incorrectly used the initial rather than the equilibrium concentrations.

b.i.Although most candidates clearly understood the concept of standard *enthalpy change of formation* many were unable to explain why the value for hydrogen is zero. Many responses neglected to mention that H_2 is an element in its standard state.

b.ii.Most candidate were able to calculate ΔH and ΔS although some inverted the equation and gave a positive value instead of negative answer or confused the values for propane and propene.

b.iii.There were some inconsistencies in the use of units and significant figures when calculating ΔG from ΔH and ΔS values although there was a significant improvement in this area compared to previous.

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b.v.There were some inconsistencies in the use of units and significant figures when calculating ΔG from ΔH and ΔS values although there was a significant improvement in this area compared to previous. This error resulted in some very strange temperatures for the thermal decomposition of propane to propene.

To determine the enthalpy change of combustion of methanol, CH_3OH, 0.230 g of methanol was combusted in a spirit burner. The heat released increased the temperature of $50.0\ cm^3$ of water from 24.5 °C to 45.8 °C.

Methanol can be produced according to the following equation.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

The manufacture of gaseous methanol from CO and H_2 involves an equilibrium reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H^\Theta < 0$$

b.i.Calculate the standard enthalpy change of this reaction, using the values of enthalpy of combustion in Table 12 of the Data Booklet. [3]

b.ii.Calculate the standard entropy change for this reaction, ΔS^Θ, using Table 11 of the Data Booklet and given: [1]

$S^\Theta(CO) = 198\ J\,K^{-1}mol^{-1}$ and $S^\Theta(H_2) = 131\ J\,K^{-1}mol^{-1}$.

b.iii.Calculate, stating units, the standard free energy change for this reaction, ΔG^Θ, at 298 K. [2]

b.iv.Predict, with a reason, the effect of an increase in temperature on the spontaneity of this reaction. [3]

c.iii.1.00 mol of CH_3OH is placed in a closed container of volume $1.00\ dm^3$ until equilibrium is reached with CO and H_2. At equilibrium 0.492 mol of CH_3OH are present. Calculate K_c. [3]

Markscheme

b.i. $CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_c^\ominus = -726\ (kJ\,mol^{-1})$

$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad \Delta H_c^\ominus = -283\ (kJ\,mol^{-1})$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H_c^\ominus = -286\ (kJ\,mol^{-1})$

*Award **[1 max]** for three correct values.*

Mark can be implicit in calculations.

$(\Delta H_R^\ominus =)\ 2(-286) + (-283) - (-726)$;

$-129\ (kJ\,mol^{-1})$;

*Award **[3]** for correct final answer.*

*Award **[2 max]** for +129 (kJ mol^{-1}).*

b.ii. $(\Delta S^\ominus = 240 - 198 - 2 \times 131 =)\ -220\ (J\,K^{-1}mol^{-1})$;

b.iii. $(-129 - 298(-0.220) =)\ -63.4\ kJ\,mol^{-1}$;

*Award **[1]** for correct numerical answer and **[1]** for correct unit if the conversion has been made from J to kJ for $\Delta S^\ominus$.*

b.iv. not spontaneous at high temperature;

$T\Delta S^\ominus < \Delta H^\ominus$ **and** $\Delta G^\ominus$ positive;

c.iii. $n(CO) = 0.508\ (mol)$;

$n(H_2) = 2 \times 0.508\ (mol)$;

$K_c \left(= \frac{0.492}{0.508 \times (2 \times 0.508)^2}\right) = 0.938$;

Accept answer in range between 0.930 and 0.940.

*Award **[3]** for correct final answer.*

*Award **[2]** for K_c = 1.066 if (c)(ii) is correct.*

Examiners report

b.i. In (i), the most common error was $+129\ kJ\,mol^{-1}$ but in (ii) the answer was often correct.

b.ii. In (i), the most common error was $+129\ kJ\,mol^{-1}$ but in (ii) the answer was often correct.

b.iii. Units tended to get muddled in (iii) and many marks were awarded as “error carried forward”.

b.iv. Few were able to explain the ΔH and $T\Delta S$ relationship in detail in (iv).

c.iii Equilibrium was well understood in general with many candidates gaining one of the two available marks. “Equal rates” was more often given than the constancy of macroscopic properties for the second mark. The K_c expression was given correctly by the vast majority of candidates (including the correct brackets and indices) but many had difficulty with the equilibrium concentrations in (iii).

The changes in equilibrium position were well understood for the most part although if a mark were to be lost it was for not mentioning the number of moles of gas.

Consider the following equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\ominus = -198\ \text{kJ mol}^{-1}$$

a.ii. State and explain the effect of increasing the pressure on the yield of sulfur trioxide. [2]

a.iv. State the effects of a catalyst on the forward and reverse reactions, on the position of equilibrium and on the value of K_c. [3]

b. When a mixture of 0.100 mol NO, 0.051 mol H_2 and 0.100 mol H_2O were placed in a $1.0\ dm^3$ flask at 300 K, the following equilibrium was established. [4]

$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$

At equilibrium, the concentration of NO was found to be $0.062\ mol\,dm^{-3}$. Determine the equilibrium constant, K_c, of the reaction at this temperature.

c.i. Outline **two** differences between an electrolytic cell and a voltaic cell. [2]

c.v. Electroplating is an important application of electrolysis. State the composition of the electrodes and the electrolyte used in the silver electroplating process. [3]

Markscheme

a.ii. yield (of SO_3) increases / equilibrium moves to right / more SO_3 formed;

3 gaseous molecules → 2 gaseous molecules / decrease in volume of gaseous molecules / fewer gaseous molecules on right hand side;

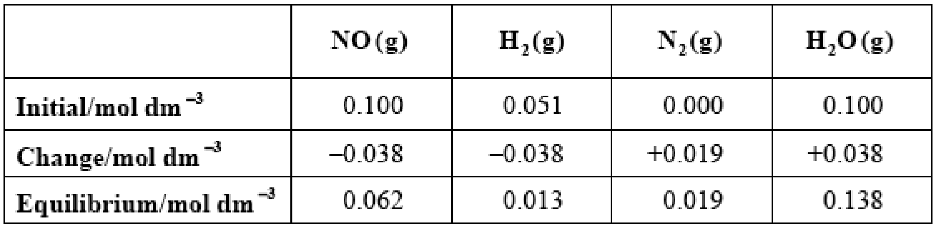
Do not allow ECF.

a.iv. rates of both forward and reverse reactions increase equally;

no effect on position of equilibrium;

no effect on value of ***[3]*** K_c;

b. $2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$



	$NO(g)$	$H_2(g)$	$N_2(g)$	$H_2O(g)$
Initial/mol dm^{-3}	0.100	0.051	0.000	0.100
Change/mol dm^{-3}	–0.038	–0.038	+0.019	+0.038
Equilibrium/mol dm^{-3}	0.062	0.013	0.019	0.138

$[H_2]$ at equilibrium $= 0.013\ (mol\,dm^{-3})$;

$[N_2]$ at equilibrium $= 0.019\ (\text{mol dm}^{-3})$;

$[H_2O]$ at equilibrium $= 0.138\ (\text{mol dm}^{-3})$;

$K_c = [N_2][H_2O]^2/[NO]^2[H_2]^2 = (0.019)(0.138)^2/(0.062)^2(0.013)^2 = 5.6 \times 10^2$;

*Award **[4]** for final correct answer.*

Accept any value also in range 557–560.

Do not penalize significant figures.

c.i. electrolytic cell converts electrical energy to chemical energy **and** voltaic cell converts chemical energy to electrical energy / electrolytic cell uses electricity to carry out a (redox) chemical reaction **and** voltaic cell uses a (redox) chemical reaction to produce electricity / electrolytic cell requires a power supply **and** voltaic cell does not;

electrolytic cell involves a non-spontaneous (redox) reaction **and** voltaic cell involves a spontaneous (redox) reaction;

in an electrolytic cell, cathode is negative and anode is positive **and** *vice-versa* for a voltaic cell / electrolytic cell, anode is positive and voltaic cell, anode is negative / electrolytic cell, cathode is negative and voltaic cell, cathode is positive;

voltaic cell has two separate solutions **and** electrolytic cell has one solution / voltaic cell has salt bridge and electrolytic cell has no salt bridge;

electrolytic cell, oxidation occurs at the positive electrode/anode **and** voltaic cell, oxidation occurs at the negative electrode/anode and *vice-versa*;

c.v. *Cathode/negative electrode*:

object to be plated;

Allow a specific example here e.g. spoon.

Accept inert metal/graphite.

Do not accept silver halides or their formulae.

Anode/positive electrode:

Silver/Ag;

Electrolyte:

$[Ag(CN)_2]^-$;

Allow silver nitrate/AgNO3 / silver cyanide/any other suitable silver salt/solution.

Do not accept AgCl.

Examiners report

a.ii. In (ii) an overwhelming number of candidates were able to score the first mark but did not refer to the gaseous state and hence lost the second mark.

a.iv. Part (iv) was another question where candidates easily scored the second and third mark. Although this has been asked a number of times in recent sessions, some candidates still do not state that the rates of both the forward and reverse reactions increase **equally**.

b. (b) was considered a very challenging question for candidates, and usually only the better candidates scored all four marks.

c.i. In (c) (i) most candidates scored two marks.

c.v. Electroplating was a topic only partially understood by candidates, and so only a few candidates obtained all three marks in (v). Often the nature of the electrode was mixed up or in many cases incorrect electrolytes were given.

Urea, $(H_2N)_2CO$, is excreted by mammals and can be used as a fertilizer.

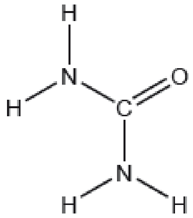
Urea can also be made by the direct combination of ammonia and carbon dioxide gases.

$$2NH_3(g) + CO_2(g) \rightleftharpoons (H_2N)_2CO(g) + H_2O(g) \quad \Delta H < 0$$

a.i. Calculate the percentage by mass of nitrogen in urea to two decimal places using section 6 of the data booklet. [2]

a.ii. Suggest how the percentage of nitrogen affects the cost of transport of fertilizers giving a reason. [1]

b. The structural formula of urea is shown. [3]



Predict the electron domain and molecular geometries at the nitrogen and carbon atoms, applying the VSEPR theory.

	Electron domain geometry	**Molecular geometry**
Nitrogen	. . . .	. . . .
Carbon	. . . .	trigonal planar

c. Urea can be made by reacting potassium cyanate, KNCO, with ammonium chloride, NH_4Cl. [2]

$$KNCO(aq) + NH_4Cl(aq) \rightarrow (H_2N)_2CO(aq) + KCl(aq)$$

Determine the maximum mass of urea that could be formed from 50.0 cm^3 of 0.100 mol dm^{-3} potassium cyanate solution.

d.i. State the equilibrium constant expression, K_c. [1]

d.ii. Predict, with a reason, the effect on the equilibrium constant, K_c, when the temperature is increased. [1]

d.iii. Determine an approximate order of magnitude for K_c, using sections 1 and 2 of the data booklet. Assume $\Delta G^\ominus$ for the forward reaction is approximately +50 kJ at 298 K. [2]

e.i. Suggest one reason why urea is a solid and ammonia a gas at room temperature. [1]

e.ii. Sketch two different hydrogen bonding interactions between ammonia and water. [2]

f. The combustion of urea produces water, carbon dioxide and nitrogen. [2]

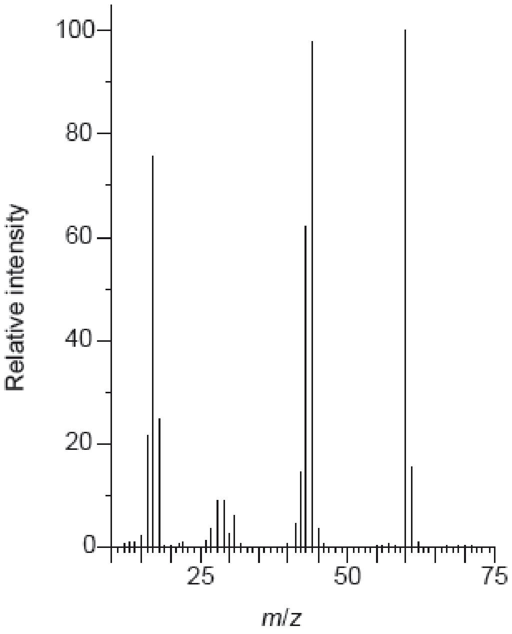
Formulate a balanced equation for the reaction.

g. Calculate the maximum volume of CO_2, in cm^3, produced at STP by the combustion of 0.600 g of urea, using sections 2 and 6 of the data booklet. [1]

h. Describe the bond formation when urea acts as a ligand in a transition metal complex ion. [2]

i. The C–N bonds in urea are shorter than might be expected for a single C–N bond. Suggest, in terms of electrons, how this could occur. [1]

j. The mass spectrum of urea is shown below. [2]



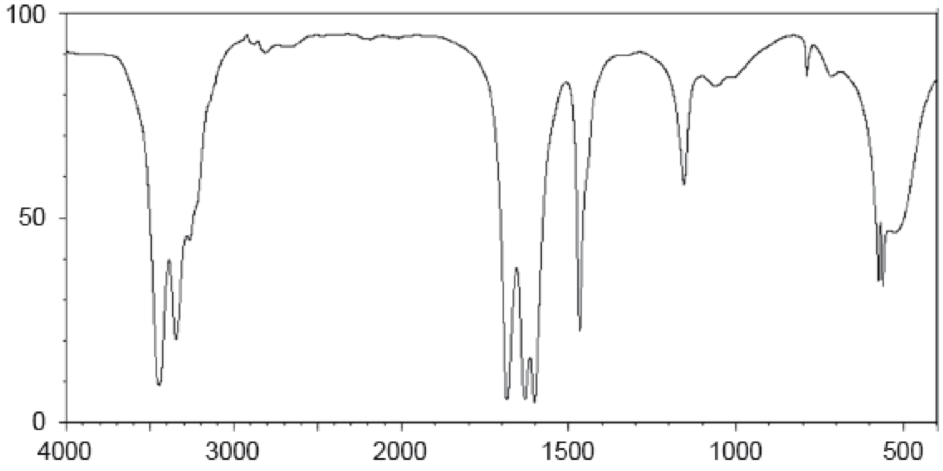
[Source: http://sdbs.db.aist.go.jp]

Identify the species responsible for the peaks at *m*/*z* = 60 and 44.

60:

44:

k. The IR spectrum of urea is shown below. [2]



[Source: sdbs.db.aist.go.jp]

Identify the bonds causing the absorptions at 3450 cm^{-1} and 1700 cm^{-1} using section 26 of the data booklet.

$3450\ \text{cm}^{-1}$:

. . . .

$1700\ \text{cm}^{-1}$:

. . . .

I.i. Predict the number of signals in the ^{1}H NMR spectrum of urea. [1]

I.ii. Predict the splitting pattern of the ^{1}H NMR spectrum of urea. [1]

I.iii. Outline why TMS (tetramethylsilane) may be added to the sample to carry out ^{1}H NMR spectroscopy and why it is particularly suited to this role. [2]

Markscheme

a.i. molar mass of urea «$4 \times 1.01 + 2 \times 14.01 + 12.01 + 16.00$» = 60.07 «g mol^{-1}»

«% nitrogen = $\frac{2 \times 14.01}{60.07} \times 100$ =» 46.65 «%»

*Award **[2]** for correct final answer.*

*Award **[1 max]** for final answer not to two decimal places.*

[2 marks]

a.ii. «cost» increases ***AND*** lower N% «means higher cost of transportation per unit of nitrogen»

OR

«cost» increases ***AND*** inefficient/too much/about half mass not nitrogen

Accept other reasonable explanations.

*Do **not** accept answers referring to safety/explosions.*

[1 mark]

b.

	Electron geometry	Molecular geometry
Nitrogen	tetrahedral ✓	trigonal pyramidal ✓
Carbon	trigonal planar ✓	trigonal planar

Note: Urea's structure is more complex than that predicted from VSEPR theory.

[3 marks]

c. n(KNCO) «= $0.0500\ \text{dm}^3 \times 0.100\ \text{mol dm}^{-3}$» = 5.00×10^{-3} «mol»

«mass of urea = $5.00 \times 10^{-3}\ \text{mol} \times 60.07\ \text{g mol}^{-1}$» = 0.300 «g»

*Award **[2]** for correct final answer.*

[2 marks]

d.i. $K_c = \frac{[(H_2N)_2CO]\times[H_2O]}{[NH_3]^2\times[CO_2]}$

[1 mark]

d.ii. «K_c» decreases ***AND*** reaction is exothermic

OR

«K_c» decreases ***AND*** ΔH is negative

OR

«K_c» decreases ***AND*** reverse/endothermic reaction is favoured

[1 mark]

d.iii. ln K « = $\frac{-\Delta G^\ominus}{RT} = \frac{-50\times10^3\ \mathrm{J}}{8.31\ \mathrm{J\ K^{-1}\ mol^{-1}}\times298\ \mathrm{K}}$ » = –20

«K_c =» 2×10^{-9}

OR

1.69×10^{-9}

OR

10^{-9}

Accept range of 20-20.2 for M1.

*Award **[2]** for correct final answer.*

[2 marks]

e.i. *Any one of:*

urea has greater molar mass

urea has greater electron density/greater London/dispersion

urea has more hydrogen bonding

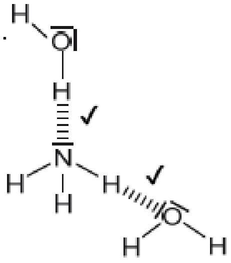
urea is more polar/has greater dipole moment

Accept "urea has larger size/greater van der Waals forces".

*Do **not** accept "urea has greater intermolecular forces/IMF".*

[1 mark]

e.ii.



*Award **[1]** for each correct interaction.*

*If lone pairs are shown on N or O, then the lone pair on N or one of the lone pairs on O **MUST** be involved in the H-bond.*

Penalize solid line to represent H-bonding only once.

[2 marks]

f. $2(H_2N)_2CO(s) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g) + 2N_2(g)$

correct coefficients on LHS

correct coefficients on RHS

Accept $(H_2N)_2CO(s) + \frac{3}{2}O_2(g) \rightarrow 2H_2O(l) + CO_2(g) + N_2(g)$.

Accept any correct ratio.

[2 marks]

g. «$V = \frac{0.600\ \text{g}}{60.07\ \text{g mol}^{-1}} \times 22700\ \text{cm}^3\ \text{mol}^{-1}$ =» 227 «cm^3»

[1 mark]

h. lone/non-bonding electron pairs «on nitrogen/oxygen/ligand» given to/shared with metal ion

co-ordinate/dative/covalent bonds

[2 marks]

i. lone pairs on nitrogen atoms can be donated to/shared with C–N bond

OR

C–N bond partial double bond character

OR

delocalization «of electrons occurs across molecule»

OR

slight positive charge on C due to C=O polarity reduces C–N bond length

[1 mark]

j. *60*: $CON_2H_4^+$

44: $CONH_2^+$

Accept "molecular ion".

[2 marks]

k. *3450 cm^{-1}:* N–H

1700 cm^{-1}: C=O

*Do **not** accept "O–H" for 3450 cm^{-1}.*

[2 marks]

l.i. 1

[2 marks]

l.ii. singlet

Accept “no splitting”.

[1 mark]

l.iii. acts as internal standard

OR

acts as reference point

one strong signal

OR

12 H atoms in same environment

OR

signal is well away from other absorptions

Accept “inert” or “readily removed” or “non-toxic” for M1.

[2 marks]

Examiners report

a.i. [N/A]
a.ii. [N/A]
b. [N/A]
c. [N/A]
d.i. [N/A]
d.ii. [N/A]
d.iii. [N/A]
e.i. [N/A]
e.ii. [N/A]
f. [N/A]
g. [N/A]
h. [N/A]
i. [N/A]
j. [N/A]
k. [N/A]
l.i. [N/A]
l.ii. [N/A]
l.iii. [N/A]

Phosgene, $COCl_2$, is usually produced by the reaction between carbon monoxide and chlorine according to the equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

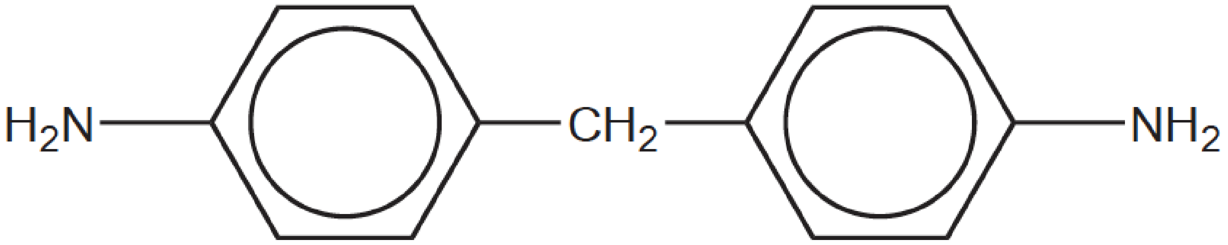
a. (i) Deduce the equilibrium constant expression, K_c, for this reaction. [8]

(ii) At exactly 600°C the value of the equilibrium constant is 0.200. Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the reaction, in kJ, using sections 1 and 2 of the data booklet. State your answer to **three** significant figures.

(iii) The standard enthalpy change of formation of phosgene, $\Delta H_f^{\ominus}$, is $-220.1\,\text{kJmol}^{-1}$. Determine the standard enthalpy change, $\Delta H^{\ominus}$, for the forward reaction of the equilibrium, in kJ, using section 12 of the data booklet.

(iv) Calculate the standard entropy change, $\Delta S^{\ominus}$, in JK^{-1}, for the forward reaction at 25°C, using your answers to (a) (ii) and (a) (iii). (If you did not obtain an answer to (a) (ii) and/or (a) (iii) use values of +20.0 kJ and −120.0 kJ respectively, although these are not the correct answers.)

b. One important industrial use of phosgene is the production of polyurethanes. Phosgene is reacted with diamine **X**, derived from phenylamine. [8]



X

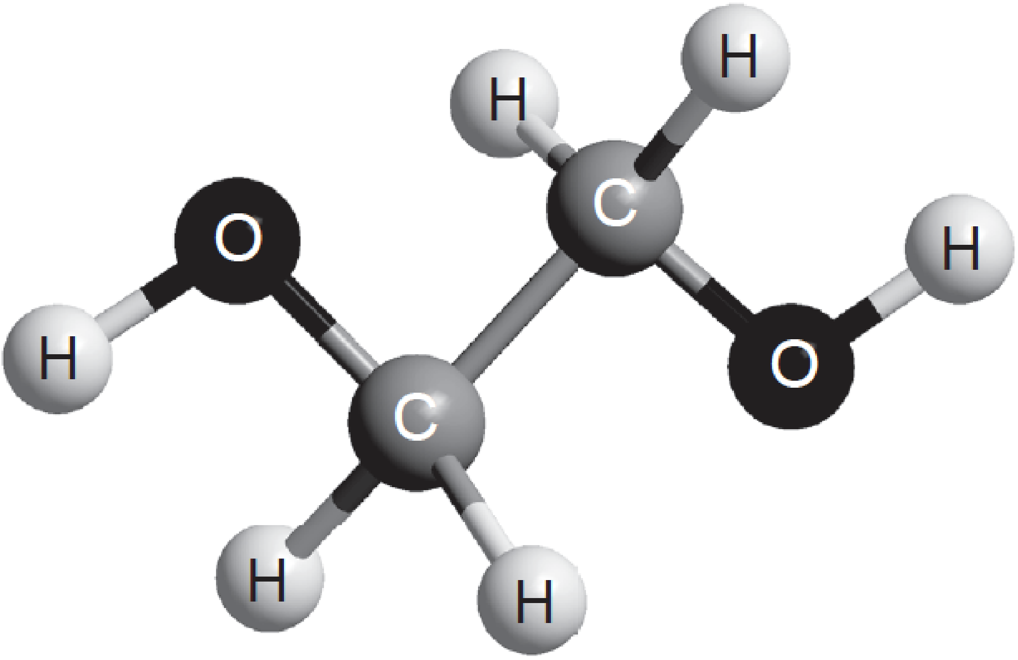
(i) Classify diamine **X** as a primary, secondary or tertiary amine.

(ii) Phenylamine, $C_6H_5NH_2$, is produced by the reduction of nitrobenzene, $C_6H_5NO_2$. Suggest how this conversion can be carried out.

(iii) Nitrobenzene can be obtained by nitrating benzene using a mixture of concentrated nitric and sulfuric acids. Formulate the equation for the equilibrium established when these two acids are mixed.

(iv) Deduce the mechanism for the nitration of benzene, using curly arrows to indicate the movement of electron pairs.

c. The other monomer used in the production of polyurethane is compound **Z** shown below. [5]



(i) State the name, applying IUPAC rules, of compound **Z** and the class of compounds to which it belongs.

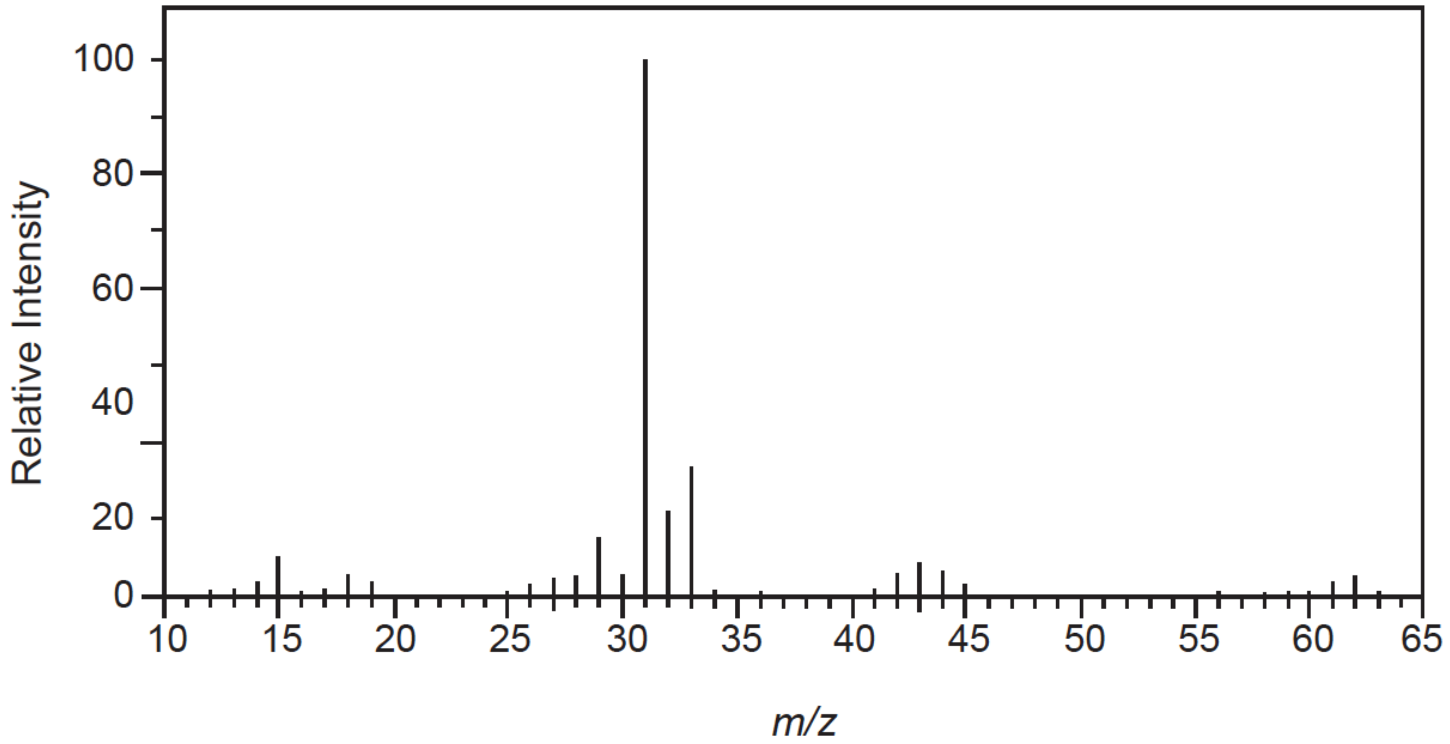
Name:

Class:

(ii) Deduce the number of signals you would expect to find in the ^{1}H NMR spectrum of compound **Z**, giving your reasons.

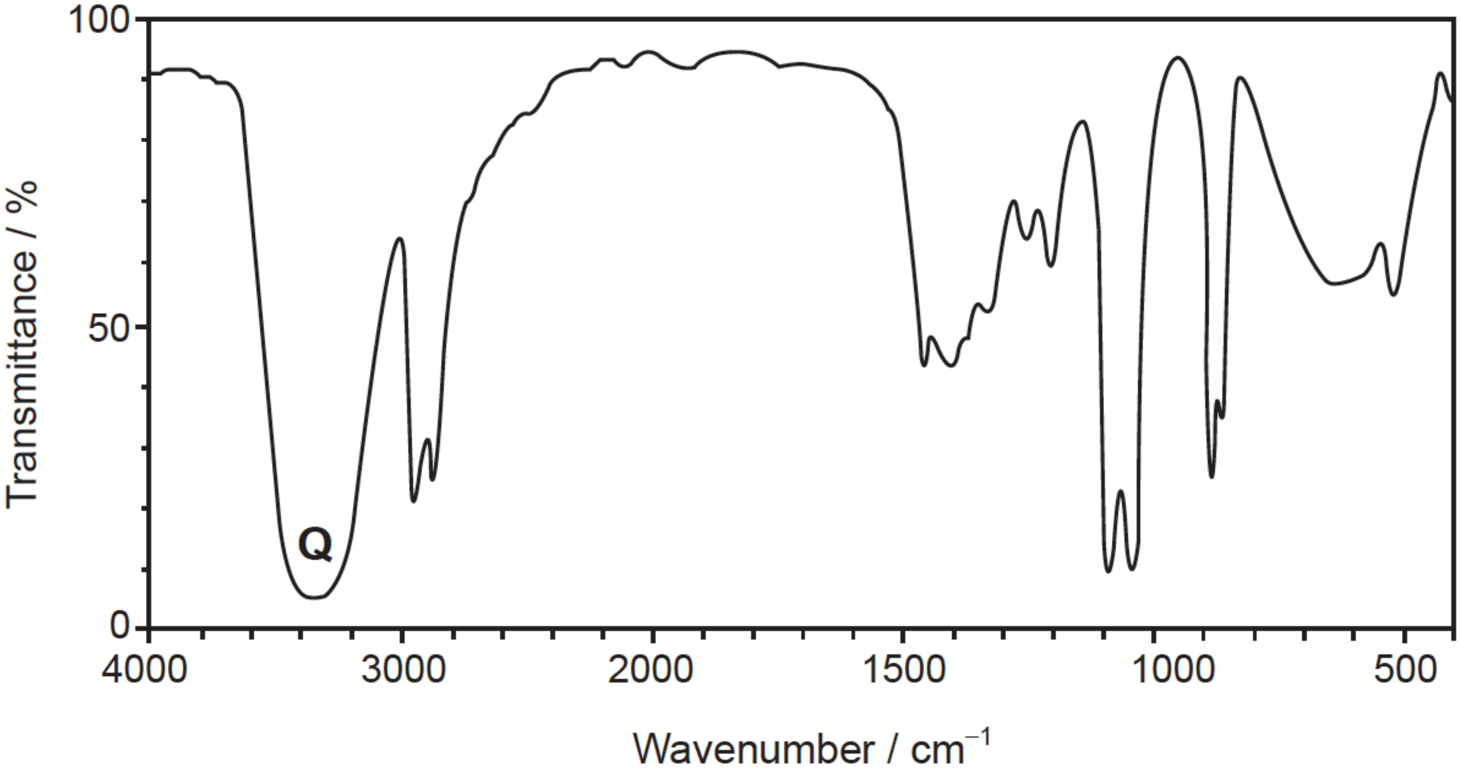
The mass spectrum and infrared (IR) spectrum of compound **Z** are shown below:

Mass spectrum



[Source: http://sdbs.db.aist.go.jp]

IR spectrum



[Source: http://sdbs.db.aist.go.jp]

(iii) Identify the species causing the large peak at *m*/*z*=31 in the mass spectrum.

(iv) Identify the bond that produces the peak labelled **Q** on the IR spectrum, using section 26 of the data booklet.

d. Phenylamine can act as a weak base. Calculate the pH of a 0.0100 mol dm^{-3} solution of phenylamine at 298K using section 21 of the data booklet. [4]

Markscheme

a. (i)

$\ll K_{\mathrm{C}}= \gg \frac{[\mathrm{COCl_2}]}{[\mathrm{CO}][\mathrm{Cl_2}]}$

(ii)
T«= 600 + 273» = 873K

$\Delta G^{\ominus} = -8.31 \times 873 \times \ln(0.200)$
OR
$\Delta G^{\ominus}$ = « + » 11676 «J»
$\Delta G^{\ominus}$ = « + » 11.7 «kJ»

Accept 11.5 to 12.0.
Award final mark only if correct sig fig.
*Award **[3]** for correct final answer.*

(iii)
$\Delta H^{\ominus} = -220.1 - (-110.5)$
$\Delta H^{\ominus}$ = –109.6 «kJ»

*Award **[2]** for correct final answer.*
*Award **[1]** for –330.6, or +109.6 «kJ».*

(iv)
$\Delta G^{\ominus} = -109.6 - (298 \times \Delta S^{\ominus}) = +11.7$ «kJ»
$\Delta S^{\ominus}$«$\frac{(11.7+109.6)\times 10^3}{298}$»= –407 «$JK^{-1}$»

*Award **[2]** for correct final answer.*
*Award **[2]** for –470 «JK^{-1}» (result from given values).*
Do not penalize wrong value for T if already done in (a)(ii).
*Award **[1 max]** for –0.407 «kJ K^{-1}».*
*Award **[1 max]** for –138.9 «J K^{-1}».*

b. (i)

primary

(ii)
ALTERNATIVE 1:
«heat with» tin/Sn ***AND*** hydrochloric acid/HCl
aqueous alkali/OH^-(aq)

ALTERNATIVE 2:

hydrogen/H_2

nickel/Ni **«catalyst»**

Accept specific equations having correct reactants.
*Do **not** accept LiAlH4 or NaBH4.*
Accept Pt or Pd catalyst.

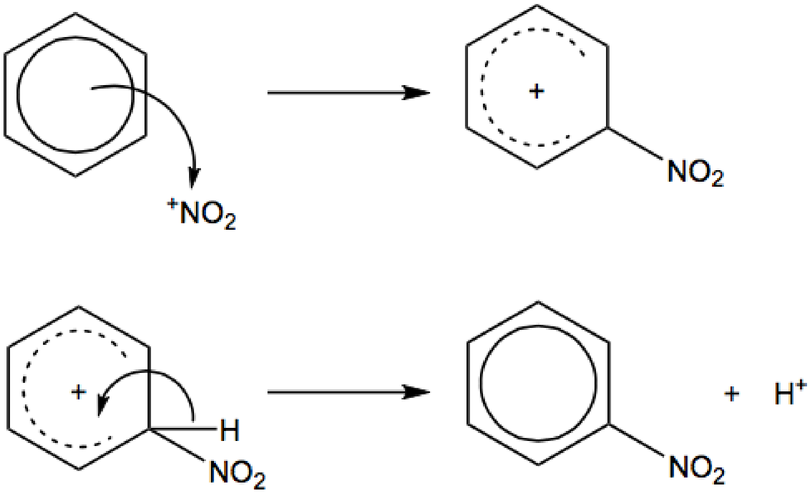
Accept equations having correct reactants.

(iii)
$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

Accept: $HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$ Accept $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$.

Accept equivalent two step reactions in which sulfuric acid first behaves as a strong acid and protonates the nitric acid, before behaving as a dehydrating agent removing water from it.

(iv)



curly arrow going from benzene ring to N of $^+NO_2/NO_2^+$

carbocation with correct formula and positive charge on ring

curly arrow going from C–H bond to benzene ring of cation

formation of organic product nitrobenzene ***AND*** H^+

Accept mechanism with corresponding Kekulé structures.

*Do **not** accept a circle in M2 or M3. Accept first arrow starting either inside the circle or on the circle.*

M2 may be awarded from correct diagram for M3.

M4: Accept $C_6H_5NO_2 + H_2SO_4$ if HSO_4^- used in M3.

c. (i)

Name: ethane-1,2-diol

Class: alcohol«s»

Accept ethan-1,2-diol / 1,2-ethanediol.

*Do **not** accept “diol” for Class.*

(ii)
two ***AND*** two hydrogen environments in the molecule
OR
two ***AND*** both CH_2 and OH present

(iii)
$^+CH_2OH$

Accept CH_3O^+.

Accept $[\bullet CH_2OH]^+$ and $[\bullet CH_3O]^+$.

Do not accept answers in which the charge is missing.

(iv)

oxygen-hydrogen «bond»/O–H «in hydroxyl»

d. $K_b \approx \frac{[OH^-]^2}{[C_6H_5NH_2]} = 10^{-9.13}/7.413 \times 10^{-10}$

$[OH^-] = \sqrt{0.0100 \times 10^{-9.13}} = 2.72 \times 10^{-6}$

$[H^+] = \frac{1\times10^{-14}}{2.72\times10^{-6}} = 3.67 \times 10^{-9}$

OR

pOH = 5.57

pH = –log $[H^+]$ = 8.44

Accept other approaches to the calculation.
*Award **[4]** for correct final answer.*
Accept any answer from 8.4 to 8.5.

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]
d. [N/A]
