Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Section A and B (Free Response) **18 September 2017**

2 hours

Additional Materials: Data Booklet
Writing Paper
Cover Sheet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.

2 Write your answers on the separate writing papers provided.

3 Write in dark blue or black pen.

4 You may use an HB pencil for any diagrams or graphs.

5 Start each question on a fresh sheet of paper.

6 At the end of the examination:

- Fasten all your work securely together with the Cover Sheet on top.

7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer **all** questions in this section.

Section B

9 Answer **one** question from this section.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

[Turn over

Section A

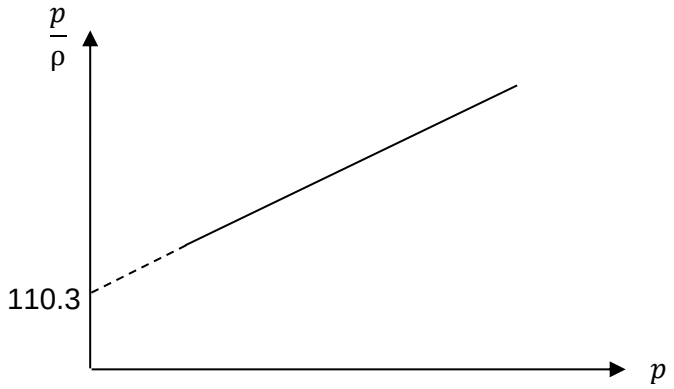
Answer **all** questions.

1 (a) Singapore has been affected by severe smoke haze due to forest fires in the region periodically. The National Environment Agency (NEA) is taking action to ensure that its population is better equipped to deal with haze.

During one of the sample analysis of air, the air sample was found to contain elevated amounts of NO_2 and gas **S**.

By careful measurements and extrapolation, the value of $\frac{p}{\rho}$ for gas **S** has been found to be approximately 110.3, at 100 °C and at very low pressure.

[p is the pressure of the gas in Pa and ρ is the density of the gas in g m^{-3}]



(i) State two main assumptions of the kinetic theory, and use these to explain why you might expect the behaviour of nitrogen dioxide to be less ideal compared to that of hydrogen. [3]

(ii) Calculate an approximate value for the relative molecular mass of **S**. [1]

(iii) Hence, identify gas **S**, where **S** is a diatomic neutral pollutant. [1]

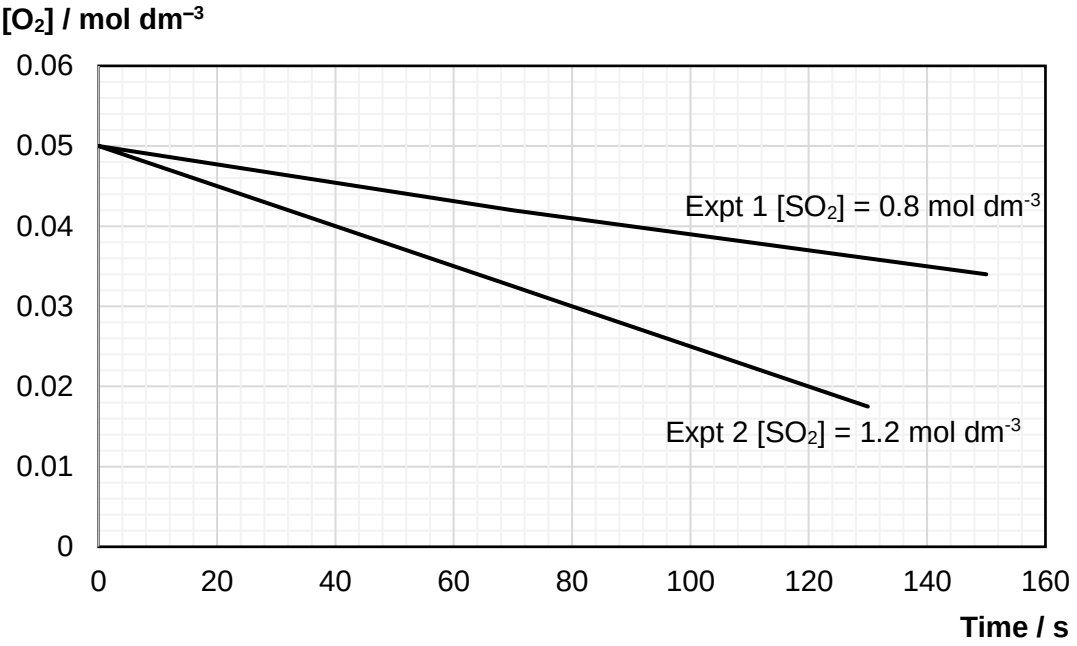
(b) Atmospheric sulfur dioxide is a major air pollutant that forms acid rain. The pollution problem caused by sulfur dioxide is amplified in the presence of atmospheric oxides of nitrogen, which act as a homogeneous catalyst.

Explain, with the aid of equation(s), how atmospheric oxides of nitrogen act as a homogeneous catalyst to amplify the pollution problems of sulfur dioxide. [3]

(c) The Contact Process is an important industrial process that occurs at 450 °C. The key stage in this process is the reaction between sulfur dioxide and oxygen.

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

Two laboratory experiments were conducted at 450 °C to investigate the kinetics of this reaction. The graph below shows the results obtained when concentrations of sulfur dioxide were varied.



(i) Use the graphs above to deduce the order of reaction with respect to sulfur dioxide and oxygen. [3]

(ii) Using one of the graphs above, calculate the value of rate constant, stating its units. [2]

(iii) Using your answer in **(i)**, sketch the graph of concentration of sulfur dioxide against time for this reaction, while keeping $[O_2]$ constant. Use construction lines to label the first and second half-lives in your sketch. [1]

(iv) Sketch and label clearly, on the same axes as in **(iii)**, how the graph would look like if the experiment was conducted at 200 °C. [1]

[Total: 15]

2 (a) Two 1.0 mol samples of hexane are mixed with separate 1.0 mol samples of cyclohexane and ethanol. The following results were obtained.

hexane mixed with	*observations*
cyclohexane	no heat is absorbed or given out
ethanol	1.0 kJ of heat is absorbed

For each mixture, consider interactions between molecules of the two liquids mixed and explain the observations. [4]

(b) In the presence of peroxides, H*X* may be added to alkenes by a free radical mechanism. The addition is said to be *anti-Markovnikov*, that is, the H atom from H*X* attaches itself to the C atom in the carbon-carbon double bond with the least number of H atoms.

The propagation steps for propene are as follows.

step 1 $CH_3CH{=}CH_2 + X\bullet \longrightarrow CH_3\overset{\bullet}{C}HCH_2X$

step 2 $CH_3\overset{\bullet}{C}HCH_2X + HX \longrightarrow CH_3CH_2CH_2X + X\bullet$

The table below shows values of the enthalpy changes, ΔH, for the propagation steps 1, 2, and for the overall reaction for H*X* respectively.

X	C*l*	Br	I
$\Delta H_{step\ 1}$ / kJ mol^{-1}	–80	–20	+20
$\Delta H_{step\ 2}$ / kJ mol^{-1}	+21	–44	–111
$\Delta H_{overall}$ / kJ mol^{-1}	–59	–64	–91

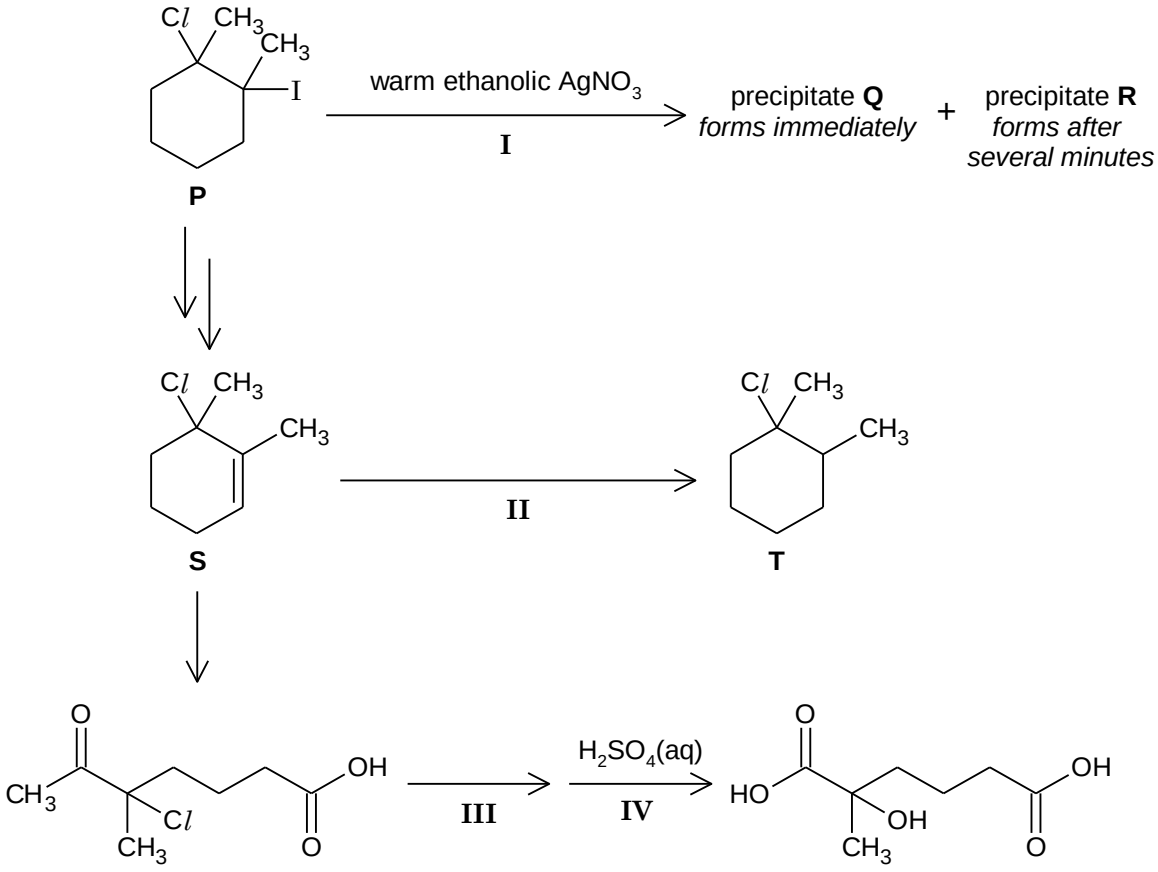
(i) By selecting relevant data from the *Data Booklet*, show that $\Delta H_{step\ 1}$ for HI and $\Delta H_{step\ 2}$ for HC*l* are +20 kJ mol^{-1} and +21 kJ mol^{-1} respectively. [2]

(ii) Experiments show that only HBr adds across an alkene via free radical mechanism.

With reference to the ΔH values given above, explain why HBr is most likely to do so and why the other two H*X* does **not** undergo the same mechanism. [2]

(iii) Hence suggest the structure of the major product formed when HI that is contaminated with small amount of peroxides is added to propene. [1]

(c) The following scheme shows the reactions of **P**, a dihalogen derivative of 1,2-dimethylcyclohexane.



(i) Identify precipitates **Q** and **R**.

With reference to the type of reaction that **P** has undergone in reaction **I**, explain the sequence in which **Q** and **R** are formed. Support your answer with suitable data from the *Data Booklet*. [3]

(ii) $LiAlH_4$ is a powerful reducing agent commonly used in organic chemistry to reduce carbonyl compounds, carboxylic acids and their derivatives. However when $LiAlH_4$ is used to reduce **S** in reaction **II**, **T** is **not** formed.

Explain these observations. [2]

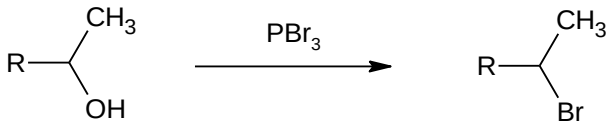
(iii) State the reagents and conditions required for reaction **III**. [1]

[Total: 15]

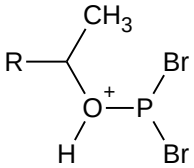
3 The chemistry of Group 15 elements, also known as Pnictogens, is discussed in this question.

(a) Common phosphorous halides contain phosphorous in oxidation states of +3 or +5 (e.g. PX_3 or PX_5). Such compounds are useful in organic or inorganic syntheses as they can function as both Lewis acids or Lewis bases.

In the synthesis of an aesthetic, Methohexital, phosphorous tribromide is used for the conversion of a secondary alcohol to an alkyl bromide.



The mechanism of the above reaction involves two steps:

step 1:	• the secondary alcohol attacks PBr_3 to form the following as an intermediate, along with a bromide ion: 
step 2: (rate-determining step)	• the bromide ion attacks the electrophilic carbon on the intermediate, facilitating the breaking of the C–O bond.

(i) Using the information given above, draw the mechanism to describe the conversion of the secondary alcohol to an alkyl bromide, showing dipoles, lone pairs, and curly arrows. [3]

(ii) State and explain if PBr_3 acts as a Lewis acid or Lewis base in the above synthesis. [1]

(iii) With reference your answer in **(i)**, explain why the reaction of phenol, instead of a secondary alcohol, with PBr_3 will result in the first step of the mechanism being relatively slower. [1]

(iv) Phenol undergoes substitution when reacted with aqueous bromine. Explain why phenol undergoes substitution instead of addition with aqueous bromine. [1]

(v) Other than using aqueous bromine or any phosphorous halides, suggest a simple chemical test to distinguish phenol from the secondary alcohol used in **(a)**.

(You can assume that the R group in the molecule does not react in any way.) [2]

(b) Both phosphorous trichloride and phosphorous pentachloride can be used in the synthesis of tricresylphosphate, a common waterproofing agent.

Phosphorous pentachloride can be formed by reacting phosphorous trichloride with chlorine gas.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 atm of PCl_3 and 1.5 atm of Cl_2 were left to equilibrate in a closed vessel at 600 K. At equilibrium, the total pressure in the vessel was determined to be 3.3 atm.

(i) Calculate the K_p of the above equlibrium. [2]

(ii) Hence, comment on the position of the equilibrium and the sign for the Gibbs free energy change of the forward reaction at 600 K. [2]

(c) The table below shows common chlorides and oxides of other Group 15 elements.

	Nitrogen	Arsenic
Chlorides	NCl_3	$AsCl_3$ $AsCl_5$
Oxides	NO N_2O NO_2	As_2O_3 As_2O_5

(i) Write an equation to show why arsenic pentachloride ($AsCl_5$) dissolves in water to give a solution with a very low pH. [1]

(ii) Draw the dot-and-cross diagram of N_2O and state its bond angle. [2]

[Total: 15]

4 The fragrance of perfume is created using a range of scents such as citrus, fresh, floral, oriental or woody. Hex-3-en-1-ol has a fresh scent with a strong 'leafy' smell of newly cut grass, Geraniol is the main ingredient of rose oil and Linalool has the scent of sweet lavender. Usually, some ethanol and water were also present in a bottle of perfume.

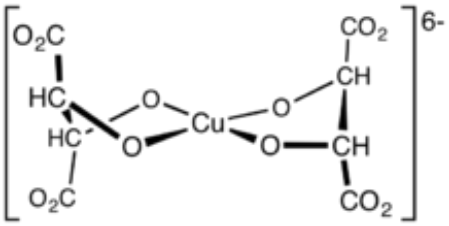
Compound	**Molecular formula**	**Structural formula**
Hex-3-en-1-ol	$C_6H_{12}O$	$CH_3CH_2CHCHCH_2CH_2OH$
Geraniol	$C_{10}H_{18}O$	$(CH_3)_2CCH(CH_2)_2C(CH_3)CHCH_2OH$
Linalool	$C_{10}H_{18}O$	$(CH_3)_2CCH(CH_2)_2C(CH_3)(OH)CHCH_2$

(a) **(i)** Geraniol and Linalool are constitutional isomers. Explain what is meant by *constitutional isomers* are. [1]

(ii) Using skeletal formula, draw the stereoisomers of hex-3-en-1-ol. [1]

(b) A compound **X**, $CH_2CCH_3(CH_2)_3C_aH_bO$, is a constitutional isomer of Geraniol. It exhibits stereoisomerism and has a particular functional group that can be tested positively by Fehling's solution, an alkaline solution of complexed $Cu^{2+}(aq)$, in a redox reaction.

In Fehling's solution, the tartrate ion forms a *complex* with Cu^{2+} as shown below.



(i) Suggest why the copper ion needs to be complexed for the test to work. [1]

(ii) Explain why such a complex can be formed between copper and tartrate ion, while no such complex is formed between potassium and tartrate ion. [2]

(iii) Suggest the structural formula of the compound **X**. [1]

(iv) A 2.0 g of fluid sample in a perfume vial containing compound **X** is treated with an excess of the Fehling's solution. The red solid obtained was collected, washed and dried. It had a mass of 0.282 g.

Given that 1 mol of **X** reacts completely with 2 mol of the Fehling's solution, calculate the percentage of compound **X** present in the fluid sample. [2]

(v) Compound **X** has a citrus scent. The human nose is able to detect the citrus scent at a minimum concentration of 10 ppm (parts per million) by mass in the air. (1 ppm by mass is 1 g in 1 x 10^6 g).

Assuming that all the fluid were vapourised, using your answer in **(iv)**, calculate the volume of a room above which the smell of compound **X** can no longer be detected by the human nose.

You may assume density of the air in the room is 1.20 kg m^{-3}. [2]

(c) When copper was added to a solution of copper(II) chloride in concentrated hydrochloric acid, a colourless solution, **Y** was obtained. During the reaction, one mole of copper(II) chloride reacts with exactly two moles of HC*l*, and no product other than compound **Y** was formed.

(i) Explain why solution **Y** is colourless. [1]

(ii) Write a balanced equation for the reaction. [1]

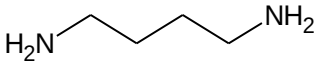
(d) When solid sodium chloride is added to a solution containing Cu^{2+}(aq), the colour changes to pale yellow-green. No such colour change occurs when solid sodium sulfate is added to Cu^{2+}(aq). Addition of water to the yellow-green solution produces the original pale blue colour. Suggest an explanation for these observations. [3]

[Total: 15]

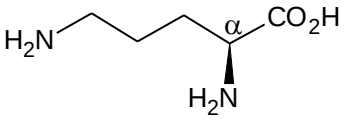
Section B

Answer **one** question from this section.

5 (a) A polyamine, butane-1,4-diamine, can be prepared from the decarboxylation of the α-COOH of an amino acid, L-ornithine, under suitable conditions.



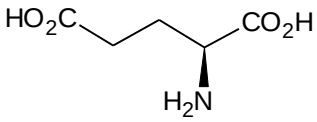
butane-1,4-diamine



L-ornithine

(i) Deduce the identity of the gaseous by-product of the reaction and hence write an equation for the formation of butane-1,4-diamine from L-ornithine. [1]

(ii) Draw and name the organic product formed when L-glutamic acid undergoes decarboxylation in a similar manner.



L-glutamic acid

[2]

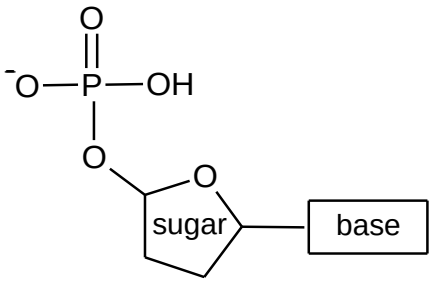
(iii) α-NH_2 and R-NH_2 of L-ornithine have different base dissociation constants, K_b.

Explain what is meant by the term K_b as applied to a weak base, **B**. [1]

(iv) State and explain how the K_b values of α-NH_2 and R-NH_2 of L-ornithine would differ. [2]

(b) Suggest a reaction scheme to synthesise butane-1,4-diamine from ethene. State the reagents and conditions required, and draw the structures of the intermediates formed. [4]

Each strand of deoxyribonucleic acid (DNA) is a macromolecule made by the polymerisation of units called nucleotides. Nucleotides are themselves made from three components (a sugar, a phosphate group and a nitrogen-containing organic base) as shown in the simplified diagram below.



Nucleotide

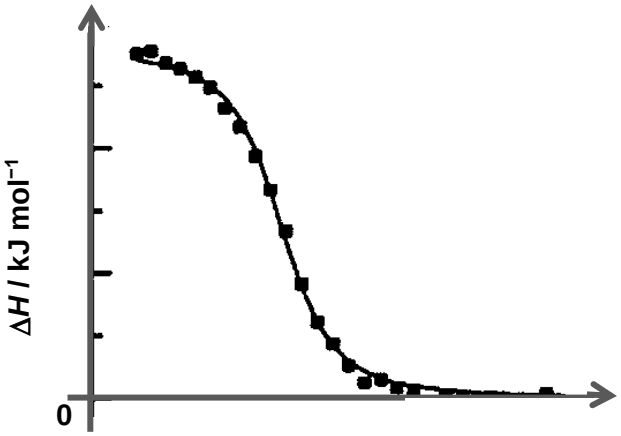
In this question, the sugar and base group remain unaltered and do not take part in any interaction.

A series of experiments was carried out in a buffer solution of pH 7.0 to investigate how butane-1,4-diamine binds with a DNA sample. The binding of butane-1,4-diamine with DNA sample occurs spontaneously.

(c) (i) Draw the predominant form of butane-1,4-diamine when it is added to the buffer solution at pH 7.0. [1]

(ii) Hence suggest the type of interaction that facilitates the binding of butane-1,4-diamine to the DNA sample. [1]

The DNA sample was dissolved in a buffer solution of pH 7.0 before it was titrated with butane-1,4-diamine at 293 K. When butane-1,4-diamine was added to the DNA sample, the following graph showing enthalpy change (kJ per mole of butane-1,4-diamine) against molar ratio (of butane-1,4-diamine to DNA sample) was obtained.



Molar ratio of butane-1,4-diamine to DNA sample

(d) (i) It is observed from the graph that the enthalpy change is zero at the higher molar ratios. Suggest why this is so. [1]

(ii) Using the graph above, deduce whether the binding of butane-1,4-diamine with the DNA sample is an endothermic or exothermic process. [1]

(iii) Using your answer in **(ii)**, deduce the sign of the entropy change when butane-1,4-diamine binds with the DNA sample. [2]

(iv) A DNA molecule is closely surrounded by water molecules upon hydration.

Use this information to suggest a reason for the sign of the entropy change in **(iii)**. [1]

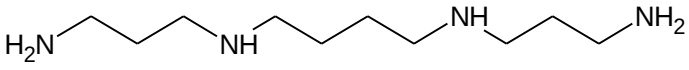
(e) The affinity of a polyamine for a DNA sample can be described by the binding constant, *K*, for the following equilibrium.

$$\text{polyamine} + \text{DNA} \rightleftharpoons \text{polyamine–DNA complex}$$

The binding constant, *K*, is further related to the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the reaction by the equation below.

$$\Delta G^{\ominus} = -RT\ln K$$

(i) Given that the numerical value of *K* for the binding between another polyamine, spermine, and the DNA sample at 290 K is 4.88×10^5, calculate the standard Gibbs free energy change in **J mol^{-1}**.



spermine

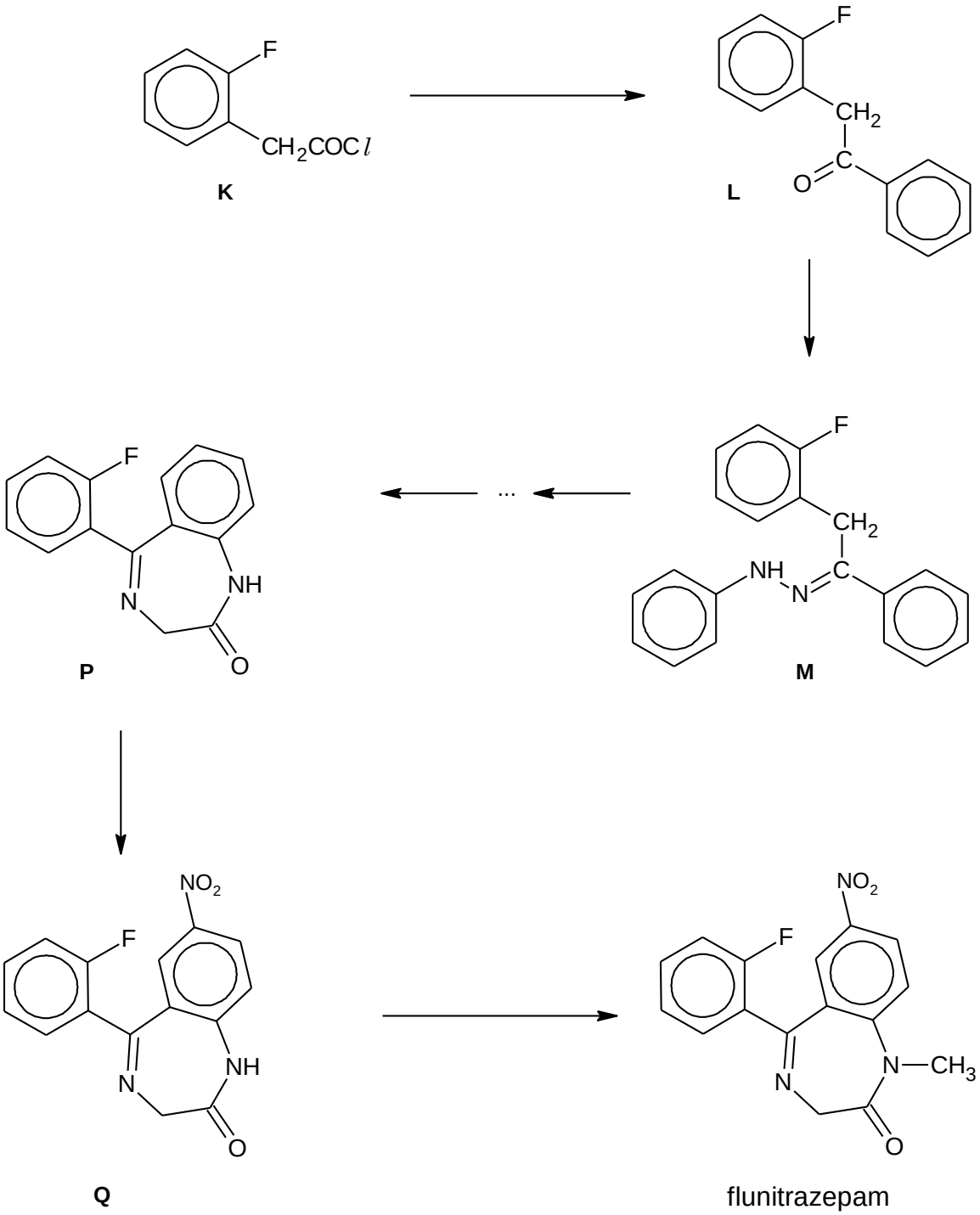
[1]

(ii) When the binding was repeated under similar conditions with butane-1,4-diamine, the standard Gibbs free energy change was found to be -2.62×10^4 J mol^{-1}.

Deduce the relative strength of interaction of the two polyamines with the same DNA sample. [2]

[Total: 20]

6 (a) Flunitrazepam is a potent sleep-inducing drug used to treat severe insomnia. Its use is under strict control in many countries. The reaction scheme below shows the synthesis of flunitrazepam from compound **K**.



(i) Propose a synthetic route, with no more than four steps, for the synthesis of **K** from 2-fluoromethylbenzene. [5]

(ii) Suggest the reagent(s) and conditions and name the type of reaction for each of the following conversions:

(I) **K** to **L**

(II) **L** to **M**

(III) **P** to **Q** [6]

(iii) The metabolism of flunitrazepam in human bodies is a first order reaction with a half-life of about 23.5 hours. Suggest an undesirable effect of using flunitrazepam as a sleep-inducing drug. [1]

(iv) A patient suffering insomnia took 1 tablet containing 1mg of flunitrazepam each night for consecutive 3 days. Assuming only about 80% of the flunitrazepam in each tablet can be absorbed by the body, estimate the mass of residual flunitrazepam in the patient's body on the 5th night. [2]

(b) Flunitrazepam acts as a sedative and hypnotic drug by enhancing the effect of the neurotransmitter γ-aminobutyric acid (GABA) at the GABA receptor in the brain. The IUPAC name of GABA is 4-aminobutanoic acid, $C_4H_9NO_2$.

(i) Explain why GABA exists as white crystalline powder. [1]

(ii) Experimentally, it is difficult to determine the melting point of GABA as it decomposes readily under high temperature to form a liquid compound, **R** of molecular formula C_4H_7NO.

By using the following thermochemical data, draw an appropriate energy cycle and calculate the standard enthalpy change of decomposition of GABA.

Standard enthalpy change of formation of solid GABA	−581.1 kJ mol^{-1}
Standard enthalpy change of formation of gaseous **R**	−197.4 kJ mol^{-1}
Standard enthalpy change of vapourisation of **R**	+73.6 kJ mol^{-1}
Standard enthalpy change of combustion of hydrogen	−286 kJ mol^{-1}

[4]

(iii) Suggest the structure of compound **R**. [1]

[Total: 20]