2023 VJC H2 Chemistry Prelim Paper 2 Answers

1 (a) State three ways in which an ideal gas differs from a real gas.

Molecules/particles of an ideal gas have zero/negligible volume. There are negligible (or NO) intermolecular forces of attraction between ideal gas molecules/particles Collisions between ideal gas molecules are perfectly elastic (i.e. no loss of energy during collision)

[3]

(b) (i) Draw a labelled diagram to show the significant force of attraction between two molecules of hydrogen fluoride. Include the name of the attraction in your diagram.



Label as hydrogen bond Lone pair and dipole

[2]

(ii) The value of pV/RT is plotted against p for 1 mol of an ideal gas and 1 mol of fluorine gas at 300 K, where p is the pressure and V is the volume of the gas.



On the same axes, sketch the variation of pV/RT against p for one mole of hydrogen fluoride, HF, at the same temperature of 300 K. Briefly explain your answer.

Correct sketch

HF deviates more from ideal behaviour because it experiences stronger intermolecular hydrogen bonding between the molecules compared to F_2 which has only instantaneous dipole–induced dipole interaction between its molecules.

[2]

[Total: 7]

2 (a) The type of bonding present in a binary compound can be predicted from the electronegativities of the elements involved. This can be shown on a van Arkel-Ketelaar triangle in **Figure 2.1**, which plots the difference in electronegativity, $\Delta \chi$, on the y-axis against the average electronegativity of the two elements, $\bar{\chi}$, on the x-axis.

In this triangle, the three corners represent the extremes of metallic, ionic, and covalent bonding, with caesium (Cs), caesium fluoride (CsF) and fluorine (F_2) at these corners.





(answer for (a)(iii)

	Position in the triangle
NaF	any point below and to the right of CsF
SiF ₄	any point below and to the right of NaF AND higher and to the left of F_2 .

(i) Describe and explain the variation in electronegativity across the third period of the Periodic Table.

<u>Electronegativity increases</u> across a period. <u>Nuclear charge increases</u> (OR number of protons increases) while <u>shielding effect is relatively</u> <u>constant</u> (OR number of inner shell electrons is the same). Hence there is an <u>increase in effective nuclear charge leading to stronger attraction</u> <u>between the nucleus and the electrons</u>, and so ability of the atom to attract electrons to itself increases. (ii) State the type of bonding present in sodium fluoride (NaF), silicon tetrafluoride (SiF₄) and the magnesium-aluminium alloy (Mg-A*l*).

Type of bonding in NaF: ionic

Type of bonding in SiF₄: **covalent**

Type of bonding in Mg-Al: metallic

[2]

(iii) Mark the approximate positions of NaF and SiF₄ on Figure 2.1

See Figure 2.1 in front

[2]

(b) Lattice energies can be obtained from constructing a Born-Haber cycle with the aid of experimental data. They can also be calculated theoretically from knowledge of the distances between the cations and anions in the crystal structure and the charge on each ion.

Table 2.1 shows the values of lattice energies for some compounds. These have been either determined from experimental data or theoretically calculated.

compound	experimental value / kJ mol ⁻¹	theoretical value / kJ mol ⁻¹
NaCl	-781	-766
NaBr	-743	-730
NaI	-699	-685
CaC <i>l</i> (non-existent compound)	_	-687
CaCl ₂	_	_
AgF	-967	-824
AgI	-889	-618

Table 2.1

Calcium(I) chloride, CaCl, is a hypothetical compound that does not exist.

(i) Define, with the aid of an equation, the lattice energy of CaCl₂.

The lattice energy of CaC l_2 refers to the <u>energy evolved</u> when <u>1 mole of</u> <u>ionic solid</u> CaC l_2 is formed from its <u>isolated gaseous ions</u> according to the equation: Ca²⁺(g) + 2C l^- (g) \rightarrow CaC l_2 (s).

(ii) The given data show the lattice energies of the sodium halides becoming less exothermic from NaC*l* to NaI.

By quoting relevant data from the *Data Booklet*, predict and explain whether you expect the lattice energy of $CaCl_2$ to be more or less exothermic than that of NaCl.

 Ca^{2+} (<u>r₊ = 0.099 nm</u>) is <u>bigger</u> than Na⁺ (<u>r₊ = 0.095 nm</u>). But CaCl₂ comprises <u>doubly-charged</u> Ca²⁺ whilst NaCl comprises <u>singly-charged Na⁺</u>. <u>Since ionic charge is the predominant factor</u> in affecting magnitude of lattice energy, the <u>lattice energy of CaCl₂ is more exothermic</u> than that of NaCl.

[2]

(iii) A larger difference between the experimental and theoretical values of the lattice energy is observed for AgI as compared to that for AgF.

Suggest why.

A greater difference between lattice energy values is observed for AgI due to a <u>more polarisable electron cloud of the anion / smaller difference in</u> <u>electronegativity between Ag and I</u>, leading to <u>greater covalent character</u>.

(iv) Using the data below as well as relevant data from **Table 2.1** and the *Data Booklet*, construct a Born-Haber cycle in the grid provided and calculate the enthalpy change of formation of solid calcium(I) chloride, CaCl(s).

Enthalpy change of atomisation of calcium = $+178 \text{ kJ mol}^{-1}$ first electron affinity of chlorine = -349 kJ mol^{-1}



energy / kJ mol⁻¹

By Hess's Law, $\Delta H_f = (+178) + (+\frac{1}{2} \times 244) + (+590) + (-349) + (-687)$ $= -146 \text{ kJ mol}^{-1}$

Equations are balanced, correct cycle and values Correct application of Hess's Law Correct answer including sign and units (v) Calcium(I) chloride is not known to exist as it readily reacts as shown in the following equation.

$$2CaCl(s) \rightarrow Ca(s) + CaCl_2(s)$$

State, with justification, the type of reaction that has occurred.

Disproportionation The oxidation state of Ca changes from +1 to 0 and +2 which shows that Ca is both reduced and oxidised.

[1]

- (c) One of the Group 2 chlorides, beryllium chloride, has many similar properties with aluminium chloride. In the vapour state at high temperatures, beryllium chloride, like aluminium chloride, exists as a dimer with the formula Be₂Cl₄. Around each beryllium atom is a trigonal planar arrangement.
 - (i) Explain how new bonds are formed two molecules of beryllium chloride during the process of dimerisation.

<u>Cl atom donates a lone pair of electrons</u> to the <u>vacant p orbital of beryllium</u>, leading to the <u>formation of a dative bond</u>.

[1]

(ii) Draw the structure of the Be_2Cl_4 dimer.



correct structure showing two dative bonds between Be and Cl.

[1]

[Total: 18]

3 Quinidine, \mathbf{Q} , ($M_r = 324.4$) is a diacidic organic base commonly used as a drug for the control of heart rhythm disturbance. Due to the low solubility of quinidine, quinidine must be fully protonated to form $\mathbf{Q}\mathbf{H}_2^{2+}$ before its concentration can be measured by carrying out a titration.

The pK_a values of the acidic groups in fully protonated quinidine are given below.

$$\mathbf{Q}\mathbf{H}_{2}^{2+} \rightleftharpoons \mathbf{Q}\mathbf{H}^{+} + \mathbf{H}^{+} \qquad \mathsf{p}K_{a1} = 4.00$$
$$\mathbf{Q}\mathbf{H}^{+} \rightleftharpoons \mathbf{Q} + \mathbf{H}^{+} \qquad \mathsf{p}K_{a2} = 8.60$$

A 10.0 cm³ sample containing 0.662 g of the fully protonated quinidine was titrated against NaOH. The first endpoint was seen after 20.00 cm³ of aqueous NaOH was added.

(a) Calculate the concentration of the fully protonated quinidine in the 10.0 cm³ sample and hence determine its pH (ignore the effects of the second acid dissociation on the pH).

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Concentration of fully protonated quinidine

= \frac{0.662}{324.4} \div 10.0 \times 1000 = 0.204 \text{ mol dm}^{-3}
K_{a1} = x^2 / (0.204 - x)
10^{-4.00} = x^2 / 0.204, \text{ assuming } x << 0.204,
x = [H^+] = (10^{-4.00} \times 0.204)^{1/2}
= 0.00452 \text{ mol dm}^{-3} \text{ (allow ecf)}
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pH = -lg 0.00452
= 2.35 (allow ecf)
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[2]

(b) (i) On the axes below, sketch a graph showing the variation of the pH of the solution as 50 cm³ of aqueous NaOH was gradually added to the 10.0 cm³ sample of protonated quinidine.

Indicate clearly

- the pH value obtained in (a),
- the pH values where maximum buffer capacity is attained, and the corresponding volumes of aqueous NaOH added.



(ii) **Table 3.1** shows some acid–base indicators together with the pH ranges over which they change colour.

name of indicator	working pH range
malachite green	0.2 – 1.8
methyl orange	3.1 – 4.4
bromothymol blue	6.0 - 7.6
thymolphthalein	9.3 – 10.6

Table	3.1	
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Name a suitable indicator that can be used to detect the second endpoint of the titration. Explain your answer.

• Thymolphthalein

• The working pH range of the indicator lies within the range of rapid pH change of the second endpoint.

[2]

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

A buffer solution is one that <u>maintains a fairly constant pH</u> when <u>small</u> <u>amounts of base or acid are added</u>.

[1]

(iv) When 8.00 cm³ of the above aqueous NaOH is added to another 10.0 cm³ sample of the above protonated quinidine solution, the resulting mixture is capable of acting as a buffer.

Explain, with the aid of two equations, the buffering action of the resulting mixture.

There is a <u>large reservoir of the QH_2^{2+} and QH^+ </u>. Hence, when a small amount of base or acid is added, $QH_2^{2+} + OH^- \rightarrow QH^+ + H_2O$ $QH^+ + H^+ \rightarrow QH^{2+}$

[2]

[Total: 10]

4 (a) At 800 K, nitrogen monoxide reacts with hydrogen according to the equation.

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(I) + N_2(g)$$

Table 4.1 shows how the initial rate of this reaction depends on the initial partial pressures of the reactants.

experiment	$p_{_{H_2}}$ / atm	$ ho_{_{NO}}$ / atm	initial rate / atm s⁻¹
1	0.64	1.60	1.50 × 10 ⁻⁷
2	0.64	0.80	3.75 × 10 ^{−8}
3	0.32	1.60	7.50 × 10 ⁻⁸

Та	b	е	4.	1

(i) Determine the order of reaction with respect to H₂ and NO. Hence state, in terms of partial pressures, the rate equation for the reaction.

From experiment 1 and 2, As $p_{_{NO}}$ halves and $p_{_{H_2}}$ is kept constant, rate decreases by 4 times.

• Hence, order wrt to NO is 2.

From experiment 1 and 3,

As p_{H_2} halves and $p_{_{NO}}$ is kept constant, rate decreases by 2 times.

• Hence, order wrt to H₂ is 1.

• rate =
$$kp_{NO}^2 p_{H_2}$$

[3]

[2]

(ii) Using the rate equation, calculate a value for the rate constant. Include units in your answer.

Experiment 1:
$$k = \frac{1.50 \times 10^{-7}}{(1.60)^2 (0.64)}$$

= • 9.16 x 10⁻⁸ • atm⁻² s⁻¹ (allow ecf)

(b) (i) Another experiment was carried out by reacting H_2 and NO at 800 K. The initial partial pressures of H_2 and NO were 0.099 atm and 2.10 atm respectively.

Calculate the time elapsed to reduce the partial pressure of H_2 to half of its initial value.

Since NO is in excess, p_{NO} is almost constant, and the reaction is pseudo 1st order wrt H₂.

Hence, rate = $k' p_{H_2}$ where $k = k p_{NO}^2$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{9.16 \times 10^{-8} \times 2.10^{2}} = 1.72 \times 10^{6} \text{ s}$$

(ii) Suggest how the time calculated in (b)(i) would change when the initial partial pressure of H₂ is doubled. Explain your answer.

• As the <u>half-life</u> of the reaction is <u>independent of the partial pressure of</u> <u>H₂</u>, the half-life of experiment 1 will <u>remain constant at 1.72×10^6 s</u>.

[1]

(c) The following mechanism has been put forward for this reaction.

Step 1 (fast) $2NO \rightleftharpoons N_2O_2$

Step 2 (slow) $H_2 + N_2O_2 \rightarrow H_2O + N_2O$

Step 3 (fast) $H_2 + N_2O \rightarrow N_2 + H_2O$

Suggest, with reasoning, whether the mechanism fits the observed kinetics data.

Since <u>Step 2</u> is the proposed slow step, rate $\propto p_{H_2} \times p_{N_2O_2}$

But N₂O₂ is an intermediate, so from <u>Step 1</u>: $p_{NO}^2 \propto p_{N_2O_2}$

 \Rightarrow rate $\propto p_{NO}^2 \times p_{H_a}$, which <u>fits the observed kinetic data</u>.

[2]

(d) The basicities of ammonia, ethylamine and phenylamine are different. Table 4.2 shows the K_b values of these three compounds.

Table 4.2

Compound	K₀ / mol dm⁻³
NH ₃	1.74 × 10 ^{–5}
CH ₃ CH ₂ NH ₂	6.40 × 10 ⁻⁴
C ₆ H ₅ NH ₂	4.30 × 10 ⁻¹⁰

(i) Explain the difference in the K_b values of these three compounds in terms of their structures.

<u>CH₃CH₂NH₂ is a stronger base</u> than NH₃ as it has an <u>electron-donating</u> <u>alkyl group</u>, which makes the <u>lone pair electrons on N more available for</u> <u>donation</u>. Thus, it has a larger K_b value than that of NH₃.

 $C_6H_5NH_2$ is a weaker base than NH_3 as the <u>lone pair electrons on N can</u> <u>delocalise into the benzene ring</u>, making it <u>less available for donation</u>. Thus, it has a smaller K_b value than that of NH_3 .

[3]

(ii) Suggest the structure formulae of the products of the following reactions.

 $C_2H_5NH_2$ + (CH₃)₂CHCOCl

C₂H₅NHCOCH(CH₃)₂ and HCl

 $C_6H_5NH_2 + Br_2(aq)$

 \mathbf{NH}_{2} Br⊳ , <mark>B</mark>r Br and HBr

[2]

[Total: 15]

5 (a) A compound S with the molecular formula C₇H₁₅Cl has one chiral carbon. An optically pure sample containing only one enantiomer of S was heated with excess aqueous KOH for a prolonged duration so that all the S initially present was completely reacted.

Upon analysis, it was found that the resulting solution does **not** rotate plane-polarised light.

(i) Based on the given information, **S** has two possible structures. Draw these two structures.



(ii) Using any one structure that you have drawn in (a)(i), outline the mechanism that has occurred in the reaction. Your answer should show clearly relevant lone pairs, dipole and curly arrows to indicate the movement of electron pairs.



[OR use the other RCl structure to draw the mechanism]

[2]

(iii) With reference to the mechanism that you have described in (a)(ii), explain why the resulting solution obtained after the reaction does not rotate plane-polarised light.

The carbocation formed after first step has a <u>trigonal planar arrangement</u> around the positively charged carbon. The <u>nucleophile attacks the</u> carbocation from either side of the plane with <u>equal probability</u>, resulting in <u>two enantiomers formed in equal proportions</u> (OR a racemic mixture), which <u>rotate plane-polarised light in opposite direction</u>. Hence, there is no net rotation overall. [Total $2\frac{1}{2}$, max 2]

(b) Organohalogen-compounds such as **S** are important in the production of quaternary ammonium compounds, QACs. The general structure of a QAC formed from a chloroalkane is shown below:



 R_1 , R_2 , R_3 and R_4 represent alkyl groups which may be the same or different from one another.

An attempt to prepare QACs was made by reacting dimethylamine, $(CH_3)_2NH$, with a 1:1 molar mixture of 1–chloropropane and 1–chlorobutane. The conditions used are such that all the $(CH_3)_2NH$ is converted to a QAC.

(i) Three possible QACs, **A**, **B** and **C**, can be formed. Draw their skeletal formulae in the space below.



(ii) Assuming that 1-chloropropane and 1-chlorobutane react with (CH₃)₂NH at the same rate, predict the ratio in which the three QACs will be formed.

Show your working and refer clearly to the structures by using the letters provided in (b)(i).

Probability of forming structure A = $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$ Probability of forming structure B = $2 \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2}$ Probability of forming structure C = $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$

Ratio of structures A : B : C = 1 : 2 : 1

(c) PCl_5 reacts with ketones in a 1 : 1 molar ratio to give gem-dichlorides. A gem-dichloride contains two chlorine atoms bonded to the same carbon atom. For example, cyclohexanone reacts with PCl_5 to give 1, 1–dichlorocyclohexane:



The carbon bonded to the two chlorine atoms is labelled 1.

(i) Suggest the phosphorus-containing by-product of this reaction.

POCl₃

[1]

(ii) When 1, 1–dichlorocyclohexane is heated with an excess of ethanolic KOH, a product T, C_6H_9Cl , is obtained and no further loss of chlorine occurs. T decolourises bromine water.

Draw the structure of T.



[1]

(iii) By considering how the type of hybridisation and the C–C–C bond angle around the carbon labelled **1** would change, suggest why the loss of both chlorine atoms does not occur.

Loss of both chlorine atoms will result in formation of either C=C=C or C=C, which will cause carbon 1 to become <u>sp hybridised</u> and the C-C-C bond angle to be <u>180°</u>. Such a compound would have too much <u>ring</u> <u>strain</u>, causing it to become unstable. Hence, loss of both chlorine atoms does not occur.

[2]

[Total: 15]

6 (a) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker. It involves the formation of an imine compound which contains a carbonnitrogen double bond:



- (i) In Step 2, the reaction proceeds via a two-stage mechanism as described below:
 - (I) protonation of the N atom in the imine by HCN to form a nucleophile and an organic intermediate.
 - (II) attack of the nucleophile on the organic intermediate to form the final product.

Draw the mechanism of the reaction occurring in Step 2. Your answer should show clearly relevant lone pairs and curly arrows to indicate the movement of electron pairs.



Stage 1: Correct structure of the organic intermediate Balanced equation

Stage 2: Lone pair on C of CN⁻ Pair of curved arrows

(ii) The synthesis of secondary amines from ketones also occurs via the formation of an imine compound.



Suggest the structure of the starting ketone and the nitrogen-containing reagent, **W**, to be used for Step 1 in the preparation of $(CH_3)_2CHNHCH_2CH_3$.

Structure of the starting ketone

о || сн₃ с _{СН3}

Nitrogen-containing reagent, W

H₂NCH₂CH₃

[2]

(iii) Ethanedioyl dichloride has the following structure:



An amine **X**, $CH_3CH(NH_2)CH_2NH_2$, reacts with ethanedioyl dichloride to produce compound **Y** with the molecular formula $C_5H_8N_2O_2$.

Write an equation for the conversion of X to Y, showing clearly the structure of Y.



(b) Valine is an essential amino acid in humans.



Table 6.1 shows some data of valine and butanedioic acid, HO₂CCH₂CH₂CO₂H:

Compound	M r	Melting point / °C
valine	117.0	298
butanedioic acid	118.0	185

Tab	le	6.	1
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Explain, with the aid of a suitable structure, why valine has a much higher melting point than butanedioic acid despite both compounds having similar M_r .

Valine exists as a <u>zwitterion</u> with the structure:

H₃N, CO₂ CH CH(CH₃)₂

Zwitterions are held by strong electrostatic forces of attractions between ions.

In contrast, butanedioic acid has a simple molecular structure consisting of discrete molecules held by <u>hydrogen bonding</u> which are much <u>weaker</u> than the ionic bonds. [Total $2\frac{1}{2}$, max 2]

(c) Chymotrypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring. For example, the tripeptide J produces two compounds K and L as shown.



The following shows the structure of a peptide containing a few amino acid residues:



Draw the two dipeptides formed when the above peptide is hydrolysed by chymotrypsin.



[2]

[Total: 10]