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CANDIDATE NAME	
CLASS	1T

CHEMISTRY

Paper 1 Multiple Choice (30 minutes) Paper 3 Free Response (1 hour) Wednesday 2 October 2019 1 hour 30 minutes

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This document consists of **11** printed pages and **1** blank page.

Paper 1



2 In an experiment, 2 moles of an aqueous metallic salt reacted exactly with 1 mole of aqueous sodium sulfite, Na₂SO₃. The half-equation for oxidation of sulfite ion, SO₃²⁻ is shown below.

 $SO_3{}^{2-}(aq) + H_2O(I) \rightarrow SO_4{}^{2-}(aq) + 2H^*(aq) + 2e^-$

If the original oxidation number of the metal in the salt was +5, what would be the new oxidation number of the metal?

A +1 B +2 C +3 D +4 Ans: D $M^{5+}: SO_3^{2-} = 2:1 \text{ (given)}$ So, $2M^{5+} \equiv SO_3^{2-} \equiv 2e^ M^{5+} \equiv e^-$ So, $M^{5+} + e^- \rightarrow M^{n+}$ n = 4, new oxidation number of the metal is +4 3 The first five successive ionisation energies of an element, **W**, found in Period 3, are as follows:

577, 1820, 2740, 11600, 14800 kJ mol⁻¹

Which statements are consistent with these data?

- 1 The outer electronic configuration of an atom of **W** is $3s^23p^1$.
- 2 There is a large increase between the 3rd and the 4th ionisation energy because the 4th electron is from an inner principal quantum shell.
- 3 W forms a chloride with a formula WCl₄.
- **A** 1 and 2 only **B** 2 and 3 only **C** 1, 2 and 3 **D** 1 only

Ans: A W is in Group 13 as there is a sharp increase between the 3rd and 4th IE. Thus, the 4th electron is found in the inner principal quantum shell and W has 3 valence electrons. Since it is in Period 3, W is aluminium. 1 The outer electronic configuration of a Group 13 element is *ns*²*np*¹. 2 True. Electrons in the inner electron shells experience less shielding effect and are nearer to the nucleus.

- 3 False. It forms chloride with molecular formula WCl₄.
- 4 The Valence Shell Electron Pair Repulsion (VSEPR) theory is used to predict the shapes of molecules.

Which shape is correctly predicted by VSEPR theory?

	Number of bo electron pairs a central ato	nded around m	Number of lor around centra	ne pairs al atom	Shape	9
A	2		1		linear	
B	2		1		trigonal pl	anar
С	3		1		tetrahed	Iral
D	3		<mark>1</mark>		trigonal pyra	amidal
	Ans: D Concepts: Using VSEPR Number of bonded	theory to p	predict shapes	of molecul	es.]
	electron pairs around central atom	Number of around c	of lone pairs central atom	s	shape	
	2		1		bent	
	3		1	trigona	I pyramidal]

5 In 1985, a molecular form of carbon, C₆₀, called buckminsterfullerene, was discovered in the products formed when graphite was vapourised. It exhibits some properties similar to graphite. The structure proposed for the molecule is a roughly spherical collection of atoms in the shape of hexagons and pentagons, very much like a soccer ball.



Which one of the following properties is expected of buckminsterfullerene?

- 1 It burns completely in oxygen to give carbon dioxide gas only.
- 2 It has a lower melting point compared to graphite.
- 3 It dissolves in water.

Α	1 only	В	2 only	C	1 and 2 o	only C	D 1,	2 and 3 c	only
A n 1. 2. 3.	 C₆₀ + 60O₂ → There are buckminsterfu buckminsterfu Buckminsterfu Buckminsterfu 	60CC weak ulleren ulleren ullerer	D ₂ intermolec e. These e has a low ne contains 6	cular fo need melting 30 C ato	orces bet little e point. ms and is r	ween mo energy t non polar.	olecules o ove Hence it	(id-id) rcome, t is insolu	of so ıble

6 Gases such as helium behave ideally under conditions of high temperature and low pressure.

Which of the following gases are very likely to behave ideally under the same conditions?

- 1 ammonia, NH₃
- 2 hydrogen, H₂
- 3 nitrogen, N₂
- A 3 only B 1 and 2 only C 2 and 3 only D 1 and 3 only



7 A student used the apparatus below to heat a can containing 300 g of water.



The following data were recorded:

Mass of propan-1-ol burnt	= <i>m</i> g
Change in temperature of water	=∆7°C

You are given that:

Relative molecular mass of propan-1-ol	= 60.0
Specific heat capacity of water	$= c J g^{-1} K^{-1}$

What is the enthalpy change of combustion, in kJ mol⁻¹, given that the process is 100 % efficient?

A
$$-\frac{m \times c \times \Delta T \times 60}{300}$$
C $-\frac{300 \times c \times \Delta T \times 60}{1000 \times m}$ B $-\frac{m \times c \times \Delta T \times 60}{1000 \times 300}$ D $-\frac{300 \times c \times (\Delta T + 273) \times 60}{1000 \times m}$

Ans: C Amount of heat energy evolved from combustion of propanol = no. of moles of propanol x ΔH_c = $\frac{m}{60.0} \times \Delta H_c$ Heat absorbed by water = mass of water x c x ΔT = $300 \times c \times \Delta T J$ = $\frac{300}{1000} \times c \times \Delta T J$ = $\frac{300}{1000} \times c \times \Delta T kJ$ $\Delta H_c = (\frac{300}{1000} \times c \times \Delta T) \div \frac{m}{60.0}$ = $\frac{300 \times c \times \Delta T \times 60}{1000 \times m}$

8 Instant heat packs comprise a supersaturated solution of sodium ethanoate and a small flat disc of iron metal embedded in the solution. Pressing the disc will cause the following reaction to occur:

$$CH_{3}CO_{2}Na(aq) + 3H_{2}O(I) \rightarrow CH_{3}CO_{2}Na.3H_{2}O(s)$$

Which of the following reflects the correct signs of ΔH , ΔS and ΔG for the overall process of the reaction?

ΔH	ΔS	ΔG
+	-	+
+	+	_
_	+	_
-	•	-
	∆H + + - <mark>-</mark>	$\Delta H \qquad \Delta S$ $+ \qquad -$ $+ \qquad +$ $- \qquad +$ $= \qquad +$

Ans: D

As the reaction is spontaneous, ΔG has a negative value. Crystallisation causes a decrease in entropy in the system, thus ΔS has a negative value. Reaction is exothermic. (Heat pack heats up, thus heat energy is released from the reaction.)

OR

Since $\Delta G = \Delta H - T\Delta S$, ΔH has to have a high negative value for reaction to be spontaneous.

9 Acrylonitrile, CH₂=CHCN, is one of the toxic and cancer-causing chemicals that was illegally dumped into a river in Pasir Gudang in March 2019.

7

CH₂=CHCN is formed industrially in the following reaction:

CH₂=CHCH₃ (g) + NH₃ (g) +
$$\frac{3}{2}$$
 O₂ (g) \implies CH₂=CHCN (g) + 3H₂O (g) Δ H = −519 kJ mol⁻¹

Which of the following changes would increase the equilibrium constant, K_{p} ?

- A adding a suitable catalyst
- **B** increasing the amount of NH₃ added
- **C** increasing the pressure

D decreasing the temperature

Ans: D (Equilibrium constant is **only affected by temperature**, hence one can decide that **D** must be the answer). A Adding a suitable catalyst will increase in the rate of reaction by increasing the rate constant, k value, and hence equilibrium will be reached faster. But does not affect equilibrium constant, K₀ as temperature remains constant. It also does not affect composition at equilibrium. В Increasing the amount of reactant, NH₃ added will shift the Position of Equilibrium (POE) to the right (so as to oppose the change and reduce the concentration of reactant), hence increasing the product formed at equilibrium, but does not affect the equilibrium constant, K_{p} as temperature remains constant. Increasing the pressure will shift the POE to the left (so as to produce less number С of moles of gas (3.5 mol of reactant vs 4 mol of product), so as to reduce pressure. This decrease the amount of product formed at equilibrium, but does not affect the equilibrium constant, $K_{\rm p}$. D Decreasing the temperature will shift the POE to the right (so as to oppose the change by releasing heat via the forward exothermic reaction). Hence increasing the amount of product formed at equilibrium, and therefore increases the equilibrium constant, $K_{\rm p}$.

10 The synthesis of ammonia gas by the Haber process is an important industrial method which leads to the production of artificial fertilisers for use in the cultivation of crops. The equilibrium reaction of the Haber Process is shown below.

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

Which of the following statements is true when the above equilibrium is subjected to a decrease in pressure?

- 1 The yield of NH₃ increases.
- 2 The amounts of N_2 and H_2 increase.
- 3 The value of K_c changes.



11 The rate of decomposition of acidified hydrogen peroxide is found to be first order with respect to the concentration of hydrogen peroxide. Which graph correctly shows how the reaction rate changes with [H₂O₂]?



12 Constitutional (structural) isomers are compounds with the same molecular formula but different arrangement of atoms.

How many constitutional isomers with molecular formula C₃H₆Br₂ are there?

A 2 B 3 C 4 D 5



13 The given diagram shows the structure of citronellol, which is used in perfumes and insect repellents.



What are the functional groups present in citronellol?

- 1 alkene
- 2 alcohol
- 3 carboxylic acid
- A 1 only
- B 1 and 2 only
- C 2 and 3 only
- **D** 1, 2 and 3



14 A catalytic converter is fitted into the exhaust system of a car for the purpose of removing toxic gases. Surfaces in a catalytic converter are coated with platinum and rhodium catalyst.

Which of the following reaction occurs in a catalytic converter?

 $\mathbf{A} \qquad \mathbf{CO}_2 + \mathbf{NO} \rightarrow \mathbf{CO} + \mathbf{NO}_2$

B $2CO + 2NO \rightarrow 2CO_2 + N_2$

- $\textbf{C} \qquad 2SO_2 + 2NO \rightarrow 2SO_3 + N_2$
- **D** $C_8H_{18} + \frac{17}{2}O_2 \rightarrow 8CO + 9H_2O$

Ans: B CO_2 and N_2 are the least harmful gases in the options. The other options are incorrect as the products, CO, NO₂ and SO₃ are toxic gases.

15 1-methylcyclohexene has the following structure:



1-methylcyclohexene

Which of the following statements is false about 1-methylcyclohexene?

- A It can react with dilute Br₂(aq).
- **B** It can react with steam in the presence of concentrated phosphoric acid to form an alcohol.
- **C** It can be reduced by hydrogen gas in the presence of nickel to form a cycloalkane.
- **D** It can be oxidised by hot concentrated acidified $KMnO_4(aq)$ to form a diol.



Paper 3

Answer **all** the questions. Write your answers on the writing paper provided. Leave <u>two lines</u> between the answers to consecutive parts of the question. Start each question on a fresh sheet of paper.

You are advised to spend **not** more than 1 hour on this paper.

1 (a) Phosphorus forms many compounds with halides that are important industrial chemicals. Three of such phosphorus halides (PX_n) are phosphorus(III) chloride, PCl₃ phosphorus(III) bromide, PBr₃ and phosphorus(III) iodide, PI₃.

The following table shows physical data on these three compounds.

	PCl ₃	PBr₃	ΡI₃
Relative molecular mass	137.5	270.7	411.7
P–X bond energy / kJ mol ⁻¹	330	270	185
Boiling point / °C	76	176	200

Use the data above to explain the following trends down the group, PCl_3 to PI_3 .

(i) decreasing P–X bond energies

The P–X bond energies decreases down the group as the <u>size of the halogen</u> atom increases from C*I* to I. The <u>valence orbitals become larger</u>, resulting in <u>less</u> <u>effective orbital overlap</u> down the group. The <u>bond length increases</u> resulting in a decreasing bond energy.

(ii) increasing boiling points of PX₃

Down the group, <u>number of electrons/size of electron cloud of phosphorus</u> <u>halide molecules increases</u> resulting in an <u>increase in the strength of the</u> <u>instantaneous dipole – induced dipole attractions</u> between the molecules, which <u>requires more energy to overcome</u>, accounting for a higher boiling point.

[2]

[3]

(b) Phosphorus(V) chloride, PC*l*₅, is another important phosphorus halide that is commonly used as a chlorinating agent in organic synthesis reactions.

In the gaseous phase, PCl_5 exists as discrete molecules.

Explain why PCl₅ does not conduct electricity in the gaseous phase.
 PCl₅ does not possess mobile charge carriers such as ions or electrons to condudt1] electricity.

In the solid crystalline phase, PCl_5 adopts an ionic structure, with the lattice consisting of two ions, PCl_4^+ and PCl_6^- .

(ii) Draw the structures of these ions and use the Valence Shell Electron Pair Repulsion (VSEPR) theory to state their shapes and bond angles. [4]

PC/4 ⁺	PC <i>l</i> ₆ ⁻	
$\begin{bmatrix} C_{l} \\ C_{l} \\ C_{l} \\ C_{l} \end{bmatrix}^{+}$	$\begin{bmatrix} Cl \\ Cl \\ Cl \end{bmatrix}$	
Shape: tetrahedral	Shape: octahedral	
Bond angle: 109 °	Bond angle: 90°	

- (c) PBr₃ is a colourless liquid with a characteristic smell. It is formed when excess solid red phosphorus reacts with liquid bromine.
 - (i) An energy level diagram is shown below, that makes use of the bond energy data in(a), the *Data Booklet* and the table below.

Enthalpy change of vaporisation of PBr ₃ (I) / kJ mol ⁻¹	+38.7
Enthalpy change of vaporisation of $Br_2(I) / kJ mol^{-1}$	+31.0
Enthalpy change of atomisation of P(s) / kJ mol ⁻¹	+314



Calculate the numerical values of the energy changes for **A**, **B** and **C** to complete the energy level diagram. [3]

A = $3/2 \times (+31) = +46.5 \text{ kJ mol}^{-1}$ **B** = $3/2 \times (+193) = +289.5 \text{ kJ mol}^{-1}$ **C** = $3 \times (+270) = +810 \text{ kJ mol}^{-1}$

(ii) Hence, use Hess' Law to determine the enthalpy change of formation for PBr₃(I). [1]

By Hess' Law, △*H*_i + 38.7 + 810 = +314 + 3/2(+31) + 3/2(+193)

 $\Delta H_{\rm f} = -198.7 \, \rm kJ \, mol^{-1}$

- (d) Ethanol, CH₃CH₂OH, which is a liquid, can be used as a source of fuel in place of hydrocarbons such as octane, C₈H₁₈.
 - (i) Define the term *standard enthalpy change of combustion* for ethanol. [1]

Standard enthalpy change of combustion of ethanol is the enthalpy change when <u>1 mole of ethanol is completely burnt in oxygen</u> under <u>standard conditions</u> of 298 K and 1 bar.

(ii) Write an equation, with state symbols, to represent the standard enthalpy change of combustion of ethanol. [1]

 $CH_3CH_2OH(I) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(I)$

(iii) Given the following data below, calculate the heat produced by complete combustion of 1 dm³ of each fuel. Hence, conclude which is a more efficient fuel based on the heat produced per dm³ of fuel.

	M r	Density / g cm ⁻³	$\Delta H_{\rm c}$ / kJ mol ⁻¹
Ethanol	46.0	0.79	-1367
Octane	114.0	0.70	-5470

1 dm³ = 1000cm³ In 1 dm³, mass of ethanol = 790 g Amount of ethanol = 790 / 46.0 = 17.173 mol

Heat produced by ethanol = $17.173 \times 1367 = 2.35 \times 10^4 \text{ kJ}$

In 1 dm³, mass of octane = 700 g Amount of octane = 700 / 114.0 = 6.14 mol Heat produced by octane = $6.14 \times 5470 = 3.36 \times 10^4 \text{ kJ}$ Given the same volume of 1 dm³, <u>octane</u> is able to produce more heat, therefore it is a more efficient fuel. 2 (a) State Le Chatelier's Principle.

Le Chatelier's Principle states that if a <u>change</u> is made to a system <u>in equilibrium</u>, the system reacts in such a way as to tend to <u>oppose the change</u>, and a <u>new</u> <u>equilibrium</u> is formed.

(b) In relation to the following equilibria,

Equilibrium 1	$2CrO_4^{2-}(aq) + 2H^+(aq) \Rightarrow Cr_2O_7^{2-}(aq) + H_2O(I);$	
Equilibrium 2	$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g);$	$\Delta H = positive$

use Le Chatelier's Principle to predict and explain the effect of

(i) increasing $[H^+(aq)]$ on *Equilibrium 1*, [1]

The position of equilibrium shifts right to decrease $[H^+(aq)]$.

(ii) increasing the pressure on *Equilibrium* 2, [1]

The <u>position of equilibrium</u> shifts <u>left</u> to <u>decrease pressure</u> by forming <u>fewer</u> <u>gaseous</u> molecules.

(iii) decreasing the temperature on *Equilibrium 2.* [1]

The position of equilibrium shifts left as the reverse reaction is exothermic and heat is released.

(c) For *Equilibrium* 3 below, when a 3:1 ratio of sulfur dioxide and oxygen at a total initial pressure of 4 atm is passed over a catalyst at a certain temperature, the partial pressure of sulfur trioxide at equilibrium is found to be 1.95 atm.

Equilibrium 3	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);$	$\Delta H = negative$
		U

(i) Calculate the partial pressures of SO₂ and O₂ at equilibrium. [1]

	2SO ₂ (g)	+	O ₂ (g)	⇒	2SO₃(g)
p _{initial} /atm	3		1		0
p _{change} /atm	- 1.95		-(0.5x1.95)		+1.95
p _{equilibrium} /atm	1.05		0.025		1.95

(ii) Hence, determine the new total pressure, and by considering the initial partial pressure of SO₂, determine also the percentage conversion of SO₂ into SO₃.

New total pressure = 1.05 + 0.025 + 1.95= 3.025 atm = 3.03 atm

% conversion of SO₂ = $\frac{1.95}{3} \times 100\%$ = 65.0%

(iii) Write an expression for the equilibrium constant, K_p , and calculate its value. Include appropriate units for K_p in your answer. [2]

$$K_{\rm p} = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 (p_{O_2})} \\ = \frac{(1.95)^2}{(1.05)^2 (0.025)} \\ = 138 \text{ atm}^{-1}$$

(iv) Any further increase in the partial pressure of SO₂ alone will not have a significant effect on the percentage conversion of SO₂ into SO₃. Suggest why this is so.

There is very little amount of O_2 left at equilibrium as compared to SO_2 .

(d) Hydrogen peroxide reacts with acidified iodide ions to liberate iodine according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(I)$$

The rate of reaction can be measured by tracking the increase in the concentration of iodine formed over time. The reaction was determined to be zero order with respect to hydrogen ions.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial [H ₂ O ₂ (aq)]	Initial [I ⁻ (aq)]	Initial rate
	/ mol dm ⁻³	/ mol dm ^{−3}	/ mol dm ⁻³ min ⁻¹
1	0.020	0.040	1.2 × 10 ⁻⁴
2	0.020	0.080	2.4 × 10 ⁻⁴
3	0.060	0.040	3.6 × 10 ⁻⁴
4	0.050	1.000	7.5 × 10⁻³

(i) Determine the order of reaction with respect to hydrogen peroxide and iodide ions, and write down the rate equation. [3] *Inspection method:*

Comparing expt. 1 & 2, keeping $[H_2O_2(aq)]$ constant, when $[I^-]$ was doubled, initial rate doubled. Hence, the reaction is first order with respect to $[I^-]$. Comparing expt. 1 & 3, keeping $[I^-(aq)]$ constant when $[H_2O_2]$ was tripled, initial rate tripled. Hence, the reaction is first order with respect to $[H_2O_2]$.

OR

Let rate= k $[H_2O_2(aq)]^m [I^-(aq)]^n$ Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ constant $\frac{1.2 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{k(0.020)^m (0.040)^n}{k(0.020)^m (0.080)^n}$ n = 1 Compare experiments 1 & 3, keeping $[I^-(aq)]$ constant $\frac{1.2 \times 10^{-4}}{3.6 \times 10^{-4}} = \frac{k(0.020)^m (0.040)^n}{k(0.060)^m (0.040)^n}$ m = 1

rate= k[H₂O₂(aq)][I⁻(aq)]

(ii) Calculate the rate constant, stating its units.

[Turn over

(iii) The reaction between hydrogen peroxide and iodide ions in acidic solution is considered to proceed via the following mechanism:

Based on your rate equation obtained in part (d)(i), state and explain which of the three steps is the rate-determining step. [2]

Step 1

In step 1, <u>**1** mol of H_2O_2 and 1 mol of I</u>⁻ reacted, which agrees with the rate equation, where the orders of reaction with respect to both H_2O_2 and I⁻ are one, respectively.

(iv) Define the term *half-life*.

[1]

It is the <u>time taken</u> for a <u>reactant's concentration to decrease to half of</u> <u>its original value</u>.

(v) In Experiment 4, the concentration of iodide ions was much greater than that of hydrogen peroxide. State the implication that this has on the kinetics of the reaction.

Since $[I^{-}(aq)] >> [H_2O_2(aq)]$, $[I^{-}(aq)]$ is approximately constant throughout the reaction. Thus, rate of reaction largely depends on $[H_2O_2]$ (a pseudo first order reaction).

rate = $k'[H_2O_2(aq)]$ where $k' = k[I^-(aq)]$

(vi) Sketch the shape of the graph of [I⁻] against time, clearly labelling the first two successive half-lives. You may use the symbols t to represent time, and c₀ to represent the initial [I⁻].

