NJC 2019 H1 Chemistry Promo Paper 2 Solutions

1 **(a)** A sample of lead contains four stable isotopes with the following percentage abundances.

Isotope	**Percentage abundance / %**
^{204}Pb	1.4
^{206}Pb	24.1
^{207}Pb	22.1
^{208}Pb	**a**

(i) Define the term *relative atomic mass*.

[1]

Relative atomic mass is the <u>weighted average isotopic mass</u> of <u>one atom</u> of an element <u>compared to $^{1}/_{12}$ the mass of a ^{12}C atom</u>.

(ii) Determine the value of **a**.
Hence calculate the relative atomic mass of lead. Give your answer to two decimal places.

[2]

% abundance of ^{208}Pb, a = 100 – 1.4 – 24.1 – 22.1 = 52.4%

Relative atomic mass of lead
= (204 × 1.4%) + (206 × 24.1%) + (207 × 22.1%) + (208 × 52.4%)
= 207.24 (2 d.p.)

<u>Examiner's comments:</u>
[1] must be 2 dp.
ECF from value of a
Some students used Pb's Ar 207.2 from Data Booklet to find the value of **a**, which is incorrect. For those who gave $gmol^{-1}$ for relative atomic mass of lead, they are penalised under units.

(iii) Bismuth is on the right side of lead in the Periodic Table. Predict and explain whether bismuth has a higher or lower first ionisation energy compared to lead.

[2]

Bi has a higher nuclear charge but same screening effect as Pb.

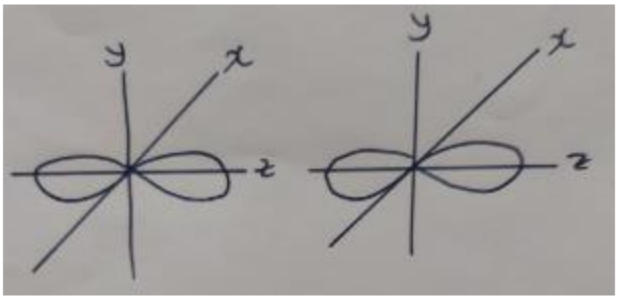
Thus there is a stronger nuclear attraction for the most loosely held electrons in Bi, more energy is required to remove the most loosely held electron in Bi.

Hence Bi has a higher first IE.

For Examiner's Use

(b) When the atomic orbitals from two atoms overlap a chemical bond may result. The p orbitals can overlap to form sigma (σ) or pi (π) bonds. When two atoms overlap the *z*-axis is used to define the internuclear axis.

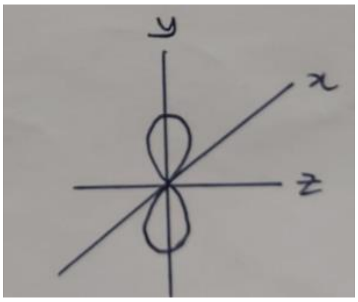
(i) On the diagram below draw two p orbitals (one orbital on each atom) that could overlap to produce a sigma (σ) bond.



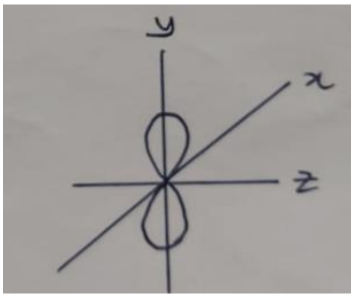
atom 1 atom 2

[1]

(ii) On the diagram below draw two p orbitals (one orbital on each atom) that could overlap to produce a **single** pi (π) bond.



atom 1



atom 2

[1]

[Total: 7]

2 One means of measuring toxicity is using LD, which stands for "Lethal Dose". LD_{50} is the amount of a material which causes the death of 50% of a group of test animals. LD_{50} value is expressed as the mass of a chemical administered per kg body mass of a test animal.

Another means of measuring toxicity is using LC, which stands for "Lethal Concentration". The concentration of the chemical in air that kills 50% of the test animals during the observation period is the LC_{50} value.

The table below shows the values for the LD_{50} and LC_{50} along with the toxicity ratings.

(1 g = 1000 mg)

Toxicity Rating	Commonly used term	LD_{50}: Oral (mg kg^{-1})	LC_{50}: Inhalation (ppm)
1	Extremely Toxic	1 or less	10 or less
2	Highly Toxic	>1 – 50	11 – 100
3	Moderately Toxic	51 – 500	101 – 1000
4	Slightly Toxic	501 – 5000	1001 – 10,000
5	Practically Non-toxic	5001 – 15,000	10,001 – 100,000

(i) 4.45×10^{-4} mol of a toxic compound, C_4H_5NO, was found to cause death in 50 % of test animals weighing 1 kg.
Calculate the LD_{50} of the compound and state its toxicity rating.

Toxicity rating:………………

[2]

Mass of compound = $4.45 \times 10^{-4} \times (48 + 5 + 14 + 16)$

= 0.03694 g

Hence, LD_{50} = **36.9 mg/kg**

The toxicity rating is **2 (highly toxic)**

(ii) Phosphine gas, PH_3, is widely used in the semi-conductor industry as a dopant.
The concentration of a small quantity of gas is usually expressed in parts per million (ppm) as shown below:

$$\text{Concentration in ppm} = \frac{\text{volume of gas}}{\text{volume of air}} \times 10^6$$

Given that the LC_{50} for PH_3 is 200 mg m^{-3} at room temperature and pressure, convert the LC_{50} to ppm and determine its toxicity rating.

Toxicity rating:………………

[3]
[Total:5]

$$\text{Volume of } PH_3 = \frac{200\ x\ 10^{-3}}{34.0} \text{ x } 24 \text{ dm}^3$$

$$= \mathbf{0.141\ dm^3}$$

$$LC_{50} = \frac{0.141\ x\ 10^{-3}}{1} \text{ x } 10^6$$

$$= \mathbf{141\ ppm}$$

The toxicity rating is **3 (moderately toxic)**.

Examiner's comments:
Many students did not get this part correct. It's either they didn't calculate the volume of PH_3 correctly or fail to do the units conversion from mg to g.

3 **(a)** Some bacteria can oxidise methane to carbon dioxide in the absence of oxygen. It has recently been reported that the mechanism involves a reaction between methane and nitrite ions in acidic conditions (reported in *Nature*, 2010).

The half-equation for the oxidation of methane is:

$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$$

(i) Write a half-equation for the reduction of NO_2^- in acidic conditions to give N_2.

…………………………………………………………………………………………………[1]

$2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4\ H_2O$

(ii) By combining the half-equations, or otherwise, balance the overall equation shown below.

……CH_4 + ……NO_2^- + ……H^+ → ……CO_2 + ……N_2 + …… H_2O

[2]

$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$ ----(1) x3

⇨ $3CH_4 + 6H_2O \rightarrow 3CO_2 + 24H^+ + 24e^-$

$2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4\ H_2O$ ----(2) x4

⇨ $8NO_2^- + 32H^+ + 24e^- \rightarrow 4N_2 + 16H_2O$

….3..CH_4 + …8…NO_2^- + ….8..H^+ → …3…CO_2 + …4…N_2 + …10… H_2O

(iii) Identify the oxidising agent in the reaction in **(ii)**. Justify your answer using oxidation numbers.

[2]

NO_2^- is the oxidising agent, itself is reduced. N is reduced from +3 in NO_2^- to zero in N_2.

[Total:5]

4 Hematite is a common iron oxide with the formula Fe_2O_3. It is a very important naturally occurring compound that finds widespread use as a heterogeneous catalyst. Fe_2O_3 is used in the Haber Process which combines nitrogen with hydrogen into ammonia.

$$N_2\,(g) + 3\,H_2\,(g) \xrightleftharpoons{Fe_2O_3} 2\,NH_3\,(g)$$

(a) **(i)** What is meant by the term ***heterogeneous*** catalyst?

[1]

The catalyst is of a different phase compared to the reactants.

(ii) State the three stages involved in a typical reaction involving a heterogeneous catalyst.

[1]

Adsorption, reaction, desorption

Examiner's Comments:

*Ad*sorption is not *ab*sorption.

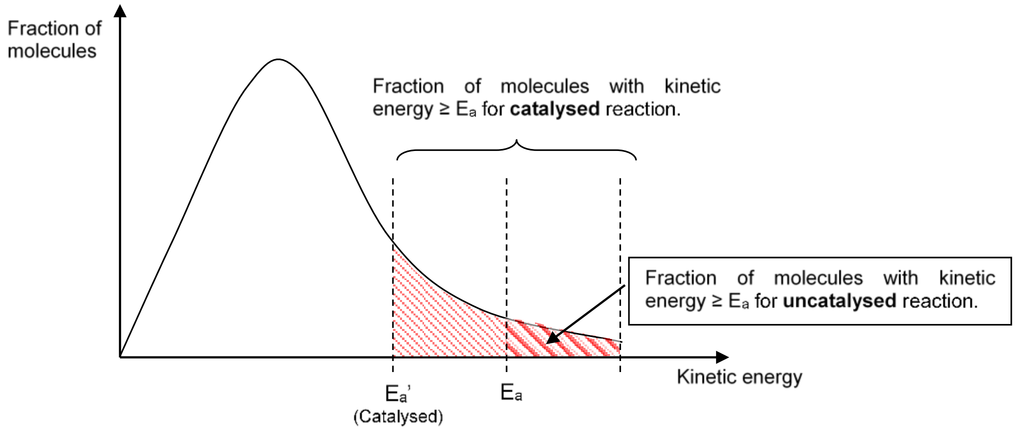
Adsorption of reactant particles onto the surface of the catalyst. **Weak interactions form between the reactant and catalyst.**

Reaction at the surface occurs at a faster rate as **reactant molecules are brought closer together** and **existing interactions in the reactant molecules are weakened** thus lowering activation energy

Desorption of products from the catalyst surface. Catalyst is regenerated.

(iii) With the aid of a Boltzman distribution curve, explain how Fe_2O_3 affect the rate of the Haber Process.

[3]



In the presence of catalyst, the reaction proceeds with an alternative reaction pathway of lower activation energy(E_a').
There are more particles with kinetic energy equal or greater than the lowered activation energy as reflected by the shaded region in the diagram above.

Frequency of effective collisions increases, leading to increase in rate of reaction.

Examiner's comments:

Generally well done.

Common mistakes:

- Not mentioning increase in frequency of effective collisions.
- Graph not starting from zero.

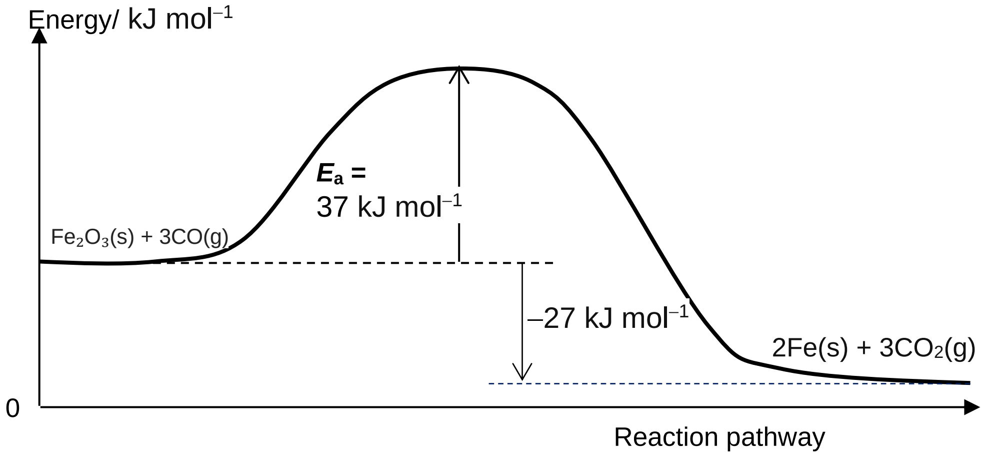
Wrongly labelled axis.

(b) Fe_2O_3 can also react with CO to produce Fe.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H_r = -27 \text{ kJ mol}^{-1}$$

(i) Draw a labelled reaction pathway diagram for this reaction, given that the activation energy of the reaction is 37 kJ mol^{-1}

[2]



(ii) Hence, or otherwise, determine the activation energy for the following reaction.

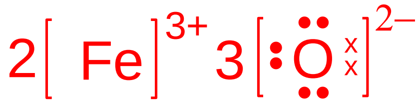
$$2Fe(s) + 3CO_2(g) \rightarrow Fe_2O_3(s) + 3CO(g)$$

[1]

37 +27 = 64 kJ mol^{-1}

(iii) Draw a dot-cross diagram to show the bonding in Fe_2O_3. Show outer electrons only.

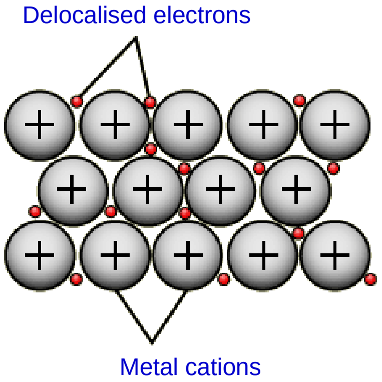
[1]



(c) **(i)** Iron is a metal.
Describe the bonding in the element iron. Draw a diagram to illustrate your answer.

[2]

Iron exhibit metallic bonding between the Fe^{2+} (Fe^{3+}) cations and the sea of delocalised electrons. [1]



[1]

(ii) State two physical properties that you would expect iron metal to possess. Explain, in terms of the bonding present, why it possesses these properties.

[2]

(ii) Property 1: High melting point

Large amount of energy is required to overcome the strong metallic bond between Fe^{2+} (Fe^{3+}) and the sea of delocalised electrons.

[1] property + explanation

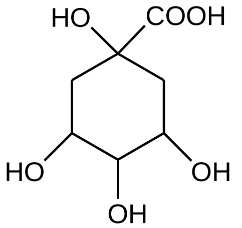
Property 2: High electrical conductivity

The sea of delocalised electrons can act as mobile charge carriers.

[1] property + explanation

[Total: 13]

5 Pure natural acids can be extracted from roasted coffee. Some are

$CH_3CH(OH)CO_2H$	$HO_2CCH{=}CHCO_2H$	CH_3COCO_2H	
Lactic acid	Maleic acid	Pyruvic acid	Quinic acid

(a) Other than the carboxylic acid functional group, what other functional groups are also present in these natural acids?

[2]

Lactic acid: alcohol/ hydroxyl group

Maleic acid: alkene

Pyruvic acid: ketone

(b) Quinic acid can be expressed as the condensed formula, $C_xH_yO_z$.

State the values for x, y and z.

x: …… y: …… z:………

[1]

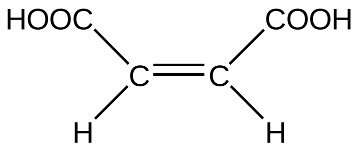
x: 7, y: 12, O: 6

(c) Maleic acid can exhibit stereoisomerism.

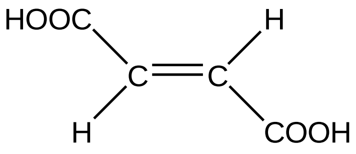
State the type of stereisomerism exhibited and draw the isomers.

[2]

Cis-trans isomerism



Cis



trans

(d) Lactic acid is able to react with aqueous NaOH in a neutralisation reaction. However, the standard enthalpy change of neutralisation between lactic acid has a smaller magnitude compared to that between hydrochloric acid and aqueous NaOH.

Explain this observation.

- HCl is a strong acids, thus completely dissociate in aqueous solution.
- Lactic acid is a weak acid, **partially dissociated** in aqueous solution. Part of the heat evolved from the neutralisation process is used to complete the dissociation of the weak acid.
  Hence the enthalpy change is **less exothermic** than that of HCl and NaOH neutralisation.

[2]

[Total:7]

6 **(a)** The kinetics of the reaction between 1-bromobutane and hydrogen sulfide ions (HS^-) was studied and the following results were obtained.

Initial concentration of 1-bromobutane /mol dm^{-3}	Initial concentration of HS^- /mol dm^{-3}	Initial rate of reaction /mol dm^{-3} s^{-1}
0.1	0.1	1.5×10^{-5}
0.2	0.1	3.0×10^{-5}
0.3	0.2	9.0×10^{-5}
x	y	4.5×10^{-5}

(i) Deduce the orders of reaction with respect to 1-bromobutane and HS^- ions.

Compare experiment 1 and 2

$\frac{[1\text{−bromobutane}]_2}{[1\text{−bromobutane}]_1} = \frac{0.2}{0.1} = 2$ and conc. of HS^- remains constant, $\frac{Rate\ 2}{Rate\ 1} = 2$

Hence order of reaction with reaction wrt 1-bromobutane is 1.

Compare experiment 1 and 3,

$$\frac{Rate\ 1}{Rate\ 3} = \frac{k[0.1][0.1]^x}{k[0.3][0.2]^x}$$

$$\frac{1.5 \times 10^{-5}}{9.0\ \times\ 10^{-5}} = \frac{k[0.1][0.1]^x}{k[0.3][0.2]^x}$$

$$x = 1$$

Order of reaction wrt HS^- is 1.

Examiner's Comments:

This question is quite well-done. Students are strongly encouraged to use mathematical deduction to determine the order wrt HS^- because there are no 2 sets of experiments with the same concentration for 1-bromobutane. Some students who tried to explain the order wrt HS^- using qualitative deduction did not give complete/sound deduction.

[2]

(ii) Hence write the rate equation and determine the rate constant of the reaction.

Rate = k[1-bromobutane][HS^-]

~~From experiment 1,~~

~~$1.5 \times 10^{-5} = k(0.1)(0.1)$~~

~~$k = 1.5 \times 10^{-3}$ mol^{-1} dm^3 s^{-1}~~

Examiner's comments:

This part is well-done, however, some students wrote the unit of k as mol^{-1} dm^3 t^{-1}.

Please note that “t” is a generic symbol to represent time which can be in second, minute or hour etc. In this question, the unit of time is specifically given as second and hence the unit for time should be in “s” instead of generic symbol “t”.

Most common mistake seen is Rate equation = k[1-bromobutane][HS^-]

[2]

(iii) Suggest a set of values for ***x*** and ***y***.

x = 0.3, y = 0.1 or any other correct mathematical combination.

Examiner’s comments:
Generally well-done. Any combination of values which results in xy = 0.03 are acceptable.

[1]

[Total:5]

7 The elements in Group 17, the halogens, and their compounds, show many similarities and trends in their properties. The table below shows the boiling points for the hydrogen halides for the elements, fluorine to iodine.

Hydrogen halide	Boiling point / K
HF	293
HC*l*	188
HBr	206
HI	238

(a) Explain the trend in the boiling points of the hydrogen halides, HF, HC*l*, HBr and HI.

More energy is required to overcome the stronger hydrogen bonding between HF molecules than Instantaneous dipole-induced dipole (idid) between molecules of HCl, HBr an HI.
From HCl to HI, electron cloud size increases, leading to increase ease of distortion. Hence tdid strength increases between the respective molecules of the hydrogen halides. More energy is needed to vaporise hydrogen halides from HCl to HI.

Examiner's comments:

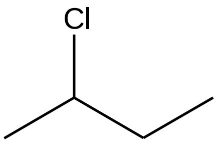
- Some students describe **hydrogen bonding** as bonds between H and F atoms in H–F molecules instead of **attractive forces between molecules**.
- Students who emphasised that "F is very electronegative and hence the **permanent dipole-permanent dipole** is very strong" is **not given any credit** as they failed to identify intermolecular force as hydrogen bonding.
- A small group of students mistook H-X to consist of H^+ ions and X^- ions. Students are to note that H-X dissociates into ions in aqueous medium due to their acidic properties, not because they are ionic compounds. **Most compounds, with the exception of ammonium salts, made of non-metals, are simple covalent molecules**.
- Another small group of students compared the H-X bond strength, quoting the bond energy values or comparing the effectiveness of orbital overlap, thinking that the covalent bonds instead of the **intermolecular forces are broken during boiling**.

[3]

(b) **(i)** Butane can react with chlorine to form 2–chlorobutane.

Draw the skeletal structure of 2–chlorobutane.

[1]



(ii) Predict and explain whether 2-chlorobutane or $(CH_3)_3CCl$ has a higher boiling point.

[2]

- 2-chlorobutane is the straight-chain isomer while $(CH_3)_3CCl$ is the branched isomer. [1/2]
- 2-chlorobutane has a higher boiling point [1] than as it has a **larger surface area of contact** between molecules [1/2] and hence more energy is required to overcome the **stronger instantaneous dipole-induced dipole interactions [1/2] between the straight-chain molecules**.

(c) Ethane and chlorine are able to react as shown below.

$$C_2H_6(g) + 2Cl_2(g) \rightarrow C_2H_4Cl_2(g) + 2HCl(g)$$

(i) Using the *Data Booklet,* determine the enthalpy change of reaction for the reaction between ethane and chlorine.

[2]

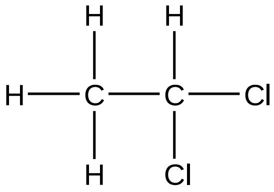
ΔH_r = [2BE(C–H) + 2BE(Cl–Cl)] – [2BE(C–Cl) + 2BE(H–Cl)]

= [2(410) + 2(244)] – [2(340) + 2(431)]

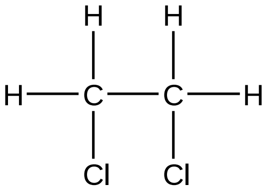
= –234 kJmol^{-1}

(ii) Draw all the possible isomers for $C_2H_4Cl_2$ and state the type of isomerism exhibited.

[2]



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & Cl & & \end{array}$$



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & Cl & & \end{array}$$

Positional / Structural Isomerism

[Total: 10]

8 Magnesium powder is used to generate heat for battlefield soldiers wanting a hot drink. 9.0 g of magnesium powder is added to 30.0 g of water.

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

(i) Calculate the volume of hydrogen gas, in dm^3, produced at room temperature and pressure.

[2]

Amount of Mg = 9.0 / 24.3 = 0.3703 mol = 0.370 mol (limiting)
Amount of water = 30.0 / 18.0 = 0.3703 mol (excess) [1]
Amt of hydrogen gas = 0.3703 mol
Volume of hydrogen gas = 0.3703 (24) = 8.89 dm^3 [1]

(iii) Using the data in the table below, calculate the standard enthalpy change of reaction for magnesium reacting with water.

substance	$\Delta H_f^{\ominus}$/ kJ mol^{-1}
H_2O	−285.8
$Mg(OH)_2$	−924.5

[2]

$\Delta H_r^{\ominus} = \Sigma\Delta H_f^{\ominus}$ (products) – $\Sigma\Delta H_f^{\ominus}$ (reactants)

$=(-924.5) - 2(-285.8) = -352.9$ kJ mol^{-1}

$= -353$ kJ mol^{-1}

(iv) Calculate the heat energy, in kJ, released when 9.0 g of magnesium powder is added to 30.0 g of water.

[1]

Heat energy = 0.370 (352.9) = 130.6 kJ = 131 kJ

(v) When the magnesium powder and water are mixed, the temperature of the drink being heated can rise to 60 °C in about 10 minutes.
Calculate how much energy, in kJ, is required to heat 150 g of the drink from 15 °C to 60 °C. Assume that the specific heat capacity of the drink is 4.2 J g^{-1}K^{-1}.

[1]

Heat required = mcΔT = 150 (4.2)(60-15) =28360 J = 28.36 kJ = 28.5 kJ

(vi) How would using 9.0 g of magnesium **granules** affect the amount of energy released and the temperature reached of the drink in about 10 minutes? Explain your answer.

[2]

Granules have a lower surface area of contact with water, thus slower rate of reaction. The same amount of heat is released as 9.0 g of Mg powder but over a longer time, thus temperature of the drink will not reach 60 °C in about 10 minutes.

[Total: 8]

End of Paper