

General Information

Instructions

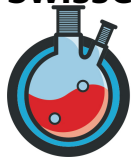
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Write all necessary calculations, ideas and explanations legibly.
- Write only in pen.
- Put your pages into the provided envelope at the end of the exam. Do not seal the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only **answers written in the given spaces** can be considered.
- The points of every exercise are weighted according to weights that can be found on the score sheet to give the final result.
- This exam has **9** problems.

Viel Erfolg!

Bonne chance!

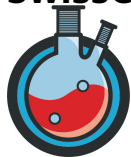
Buona fortuna!

Good luck!

**Physical Constants and Formulae****Constants**

Planck constant	$h = 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$
Speed of light	$c = 2.997 \times 10^8 \text{ m s}^{-1}$
Elementary charge	$e = 1.602 \times 10^{-19} \text{ C}$
Avogadro's constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Faraday constant	$F = 9.648 \times 10^4 \text{ C mol}^{-1}$
Standard pressure	$p_0 = 1 \times 10^5 \text{ Pa}$
Electronvolt	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
Absolute zero	$0 \text{ K} = -273.15 \text{ }^\circ\text{C}$
Ångstrom	$1 \text{ Å} = 1 \times 10^{-10} \text{ m}$
Pi (π)	$\pi \approx 3.141592$
Euler's number	$e \approx 2.718281$

For the calculation of equilibrium constants and all concentrations, refer to the standard concentration $1 \text{ mol dm}^{-3} = 1 \text{ mol L}^{-1}$. If not stated otherwise in a task, consider all gases ideal throughout this exam.



Formulae and Equations

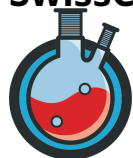
Ideal gas law	$pV = nRT = Nk_B T$
Gibbs free energy	$\Delta G = \Delta H - T\Delta S$
Relation between ΔG° and K	$\Delta G^\circ = -RT \ln(K)$
Relationship between ΔG and ΔE_{cell}	$\Delta G = -zF\Delta E_{\text{cell}}$
Nonstandard ΔG	$\Delta_r G = \Delta_r G^\circ + RT \ln(Q)$
Reaction quotient Q for reaction $aA + bB \rightleftharpoons cC + dD$	$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
Nernst equation	$E = E^\circ - \frac{RT}{zF} \ln(Q)$
Arrhenius law	$k = Ae^{-\frac{E_a}{RT}}$
Electric current	$I = \frac{q}{t}$
Lambert-Beer law	$A = \epsilon Lc = \log\left(\frac{I_0}{I}\right)$
Buffer equation	$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
Definition of pK_a	$\text{pK}_a = -\log\left(\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}\right)$
Energy of a photon	$E = h\nu = \frac{hc}{\lambda}$
Half life of a first-order reaction	$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$
Activity of a radioactive sample	$A = kN$
Surface area of a sphere	$A = 4\pi R^2$
Volume of a sphere	$V = \frac{4}{3}\pi R^3$



Periodic Table of Elements

1 H 1.008																		2 He 4.003																	
3 Li 6.94		4 Be 9.01																		9 F 19.00															
11 Na 22.99		12 Mg 24.31																		17 Cl 35.45															
19 K 39.10		20 Ca 40.08		21 Sc 44.96		22 Ti 47.87		23 V 50.94		24 Cr 52.00		25 Mn 54.94		26 Fe 55.85		27 Co 58.93		28 Ni 58.69		29 Cu 63.55		30 Zn 65.38		31 Ga 69.72		32 Ge 72.63		33 As 74.92		34 Se 78.97		35 Br 79.90		36 Kr 83.80	
37 Rb 85.47		38 Sr 87.62		39 Y 88.91		40 Zr 91.22		41 Nb 92.91		42 Mo 95.95		43 Tc [98]		44 Ru 101.07		45 Rh 102.91		46 Pd 106.42		47 Ag 107.87		48 Cd 112.41		49 In 114.82		50 Sn 118.71		51 Sb 121.76		52 Te 127.60		53 I 126.90		54 Xe 131.29	
55 Cs 132.91		56 Ba 137.33		57-71 La 57.71		72 Hf 178.49		73 Ta 180.95		74 W 183.84		75 Re 186.21		76 Os 190.23		77 Ir 192.22		78 Pt 195.08		79 Au 196.97		80 Hg 200.59		81 Tl 204.38		82 Pb 207.2		83 Bi 208.98		84 Po [209]		85 At [210]		86 Rn [212]	
87 Fr [223]		88 Ra [226]		89-103 Ac 89-103		104 Rf [267]		105 Db [268]		106 Sg [269]		107 Bh [270]		108 Hs [270]		109 Mt [278]		110 Ds [281]		111 Rg [282]		112 Cn [285]		113 Nh [286]		114 Fl [289]		115 Mc [290]		116 Lv [293]		117 Ts [294]		118 Og [294]	

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac [227]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [266]



Score Sheet

Not to be filled in by the student.

Student's name: _____

Q	Title	Points	Weight
1	Basics of Chemistry?	18.5	8%
2	Acids: From Filthy Foul to Fruitily Fragrant	14.0	9%
3	Redox Chemistry with KMnO_4	13.5	11%
4	Iodine: Quiet or Explosive	17.0	13%
5	Luminol Literally Lighting Labs	13.0	10%
6	Carbon Clock: Archeology and <i>in vivo</i> Imaging	16.0	15%
7	Gaslighting and Lighting Gasses	12.5	11%
8	Tasting the Right (and Left) Sugars	16.0	11%
9	Organic Reactions	13.0	9%
Σ	TOTAL		100%

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Σ	TOTAL		100%



Basics of Chemistry?

(18.5 pts, 8%)

1.1 Indicate whether the following processes include chemical reactions.

2.0 pt

SOLUTION:

Charging your phone	☒ Yes	☐ No
Boiling salt water	☐ Yes	☒ No
Electromagnets lifting iron	☐ Yes	☒ No
Baking cookies	☒ Yes	☐ No

0.5 pts for each correct answer.
No points for unclear/multiple answers.
2.0 pts total.

1.2 Indicate, for the following four properties, whether the trend follows $I > Br > Cl > F$.

2.0 pt

SOLUTION:

Electronegativity	☐ Yes	☒ No
Atomic radius	☒ Yes	☐ No
Acidity (of HX)	☒ Yes	☐ No
Boiling point (of X_2)	☒ Yes	☐ No

0.5 pts per correct answer.
0.0 pts if the answer is wrong/unclear/both marked.
2.0 pts total.

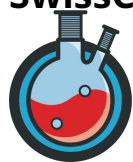
1.3 Select the element with the highest atomic mass.

1.0 pt

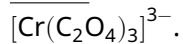
SOLUTION:

☐ Samarium (Sm) ☐ Curium (Cm) ☐ Hafnium (Hf) ☒ Meitnerium (Mt)

1.0 pts for the correct answer.
1.0 pts total.



1.4 **Select** the number of oxygen atoms in one mole of tris(oxalato)chromate(III) 1.0 pt



SOLUTION:

☐ 2.409×10^{24}

☒ 7.227×10^{24}

☐ 1.807×10^{24}

☐ 6.022×10^{23}

The result is obtained by multiplying the number of oxygen atoms per unit of

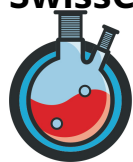
$[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (12 O) times Avogadro's constant $N_A = 6.022 \times 10^{23}$.

$$12 \cdot N_A = 12 \cdot 6.022 \times 10^{23} = 7.227 \times 10^{24}.$$

1.0 pts for the correct answer.

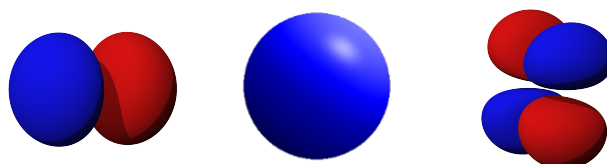
No partial point for unclear/multiple answers.

1.0 pts total.



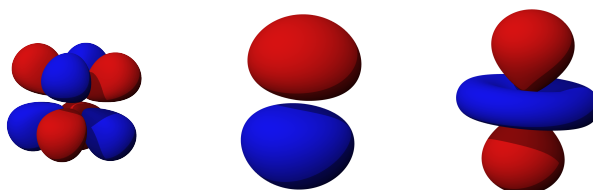
1.5 Select the orbital type of each illustration.

3.0 pt



SOLUTION:

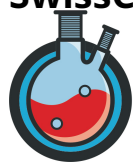
☐ s	☒ s	☐ s
☒ p	☐ p	☐ p
☐ d	☐ d	☒ d
☐ f	☐ f	☐ f



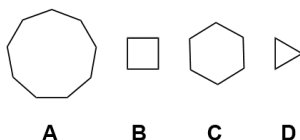
SOLUTION:

☐ s	☐ s	☐ s
☐ p	☒ p	☐ p
☐ d	☐ d	☒ d
☒ f	☐ f	☐ f

0.5 pts for each correctly assigned orbital.
No points for unclear/multiples assignments.
3.0 pts total.



- 1.6 **Order** the following cycloalkanes **A-D** with increasing ring strain (from least to most strained). 1.0 pt



SOLUTION:

☐ **D<B<A<C**

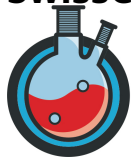
☐ **A<C<B<D**

☒ **C<A<B<D**

☐ **B<D<A<C**

1.0 pts for correct answer.

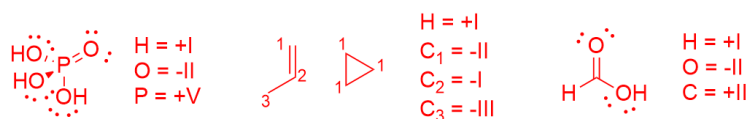
1.0 pts total.



1.7 **Draw** a stable Lewis formula of the following sum formulae and **determine** the oxidation states of all atoms. 4.5 pt

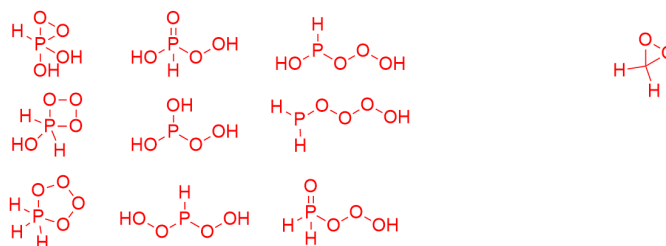
SOLUTION:

Correct structures with their oxidation states:



Although lone pairs belong to complete Lewis structures, full marks are also awarded for consistently omitted lone pairs. Points are deducted for incorrect lone pairs (too many/too few or on the wrong atom).

The following are questionable structures, which follow the sum formula. All oxygen atoms possess two lone pairs.



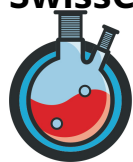
1.0 pts for each stable chemical structure that follows the sum formula.

0.5 pts/1.0 pts if the sum formula is matched, but the structure is questionable.

0.5 pts/1.0 pts if the sum formula is matched, but lone pairs are wrong (missing is acceptable in this case).

0.5 pts for the correct oxidation state of all atoms for a drawn structure.

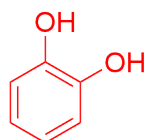
4.5 pts total.



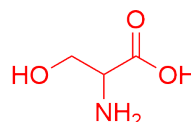
1.8 **Complete** the structures according to IUPAC nomenclature.

4.0 pt

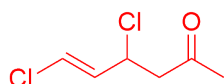
SOLUTION:



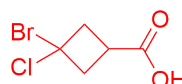
Benzene-1,2-diol ($C_6H_6O_2$)



2-Amino-3-hydroxypropanoic acid ($C_3H_7O_3N$)



4,6-Dichlorohex-5-en-2-one
($C_6H_8OCl_2$)

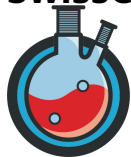


3-Bromo-3-chlorocyclobutane-1-carboxylic acid
($C_4H_6O_2ClBr$)

1.0 pts per correct structure.

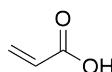
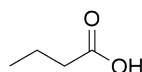
0.5/1.0 pts if too much/little was added, but there is at least one correct "functional group".

4.0 pts total.



Acids: From Filthy Foul to Fruitily Fragrant (14.0 pts, 9%)

Carboxylic acids appear commonly in everyday life. Many of these short-chained carboxylic acids have unique tastes or odours. Let us first discuss three such carboxylic acids: acetic acid **HA** (smells like vinegar), acrylic acid **HB** (smells like acrid, burnt oil) and butyric acid **HC** (smells like aged cheese or vomit). The strength of these acids is given by their pK_a value. For most carboxylic acids such these three, pK_a values hover around 4.50.

**HA** $pK_a = 4.76$ $M_{HA} = 60 \text{ g} \cdot \text{mol}^{-1}$ **HB** $pK_a = 4.25$ $M_{HB} = 72 \text{ g} \cdot \text{mol}^{-1}$ **HC** $pK_a = 4.82$ $M_{HC} = 88 \text{ g} \cdot \text{mol}^{-1}$

- 2.1** Give the balanced equation for the deprotonation reaction of acetic acid **HA** with NaOH. Use the structural formula in your representation of **HA**. 1.0 pt

SOLUTION:



Any reasonable solution that is correct, regardless of equilibrium arrow or monodirectional arrow.

1.0 pts for correct and fully balanced equation, if structure or formula is correct.

0.5 pts/1.0 pts if they use "HA" instead of the structure.

1.0 pts total.

- 2.2** Order the acids **HA**, **HB**, and **HC** in order of increasing acid strength. 1.0 pt

SOLUTION:



The lower the pK_a , the stronger the acid.

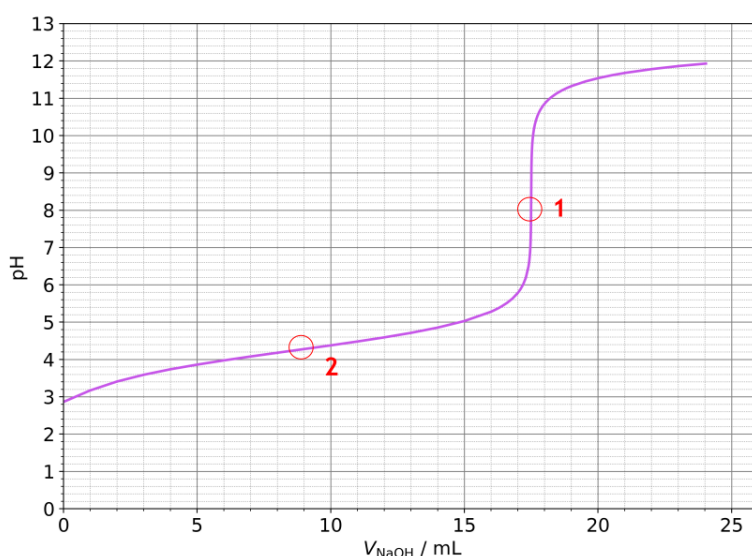
1.0 pts for correct ordering. No partial points for wrong order.

1.0 pts total.



You find an unlabelled bottle in your lab that contains a solution of one of the three acids **HX** (either **HA**, **HB** or **HC**). With your trusty pH meter, you titrate a sample with a volume $V_{\text{sample}} = 50 \text{ mL}$ of the unknown solution of **HX** with NaOH ($c_{\text{NaOH}} = 0.100 \text{ mol L}^{-1}$) and get the following titration curve.

SOLUTION:



2.3 On the titration curve, **mark** a cross at the following points (no geometric determination/precision necessary): 2.0 pt

- Equivalence point (**mark** with "1")
- Half-equivalence point (**mark** with "2")

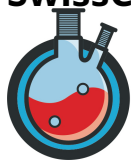
SOLUTION:

The equivalence point (1) and half-equivalence point (2) are marked. Any markings in the respective approximate areas will be counted.

1.0 pts for each correct marking.

If the two points are swapped, 1.0 pts/2.0 pts total are awarded.

2.0 pts total.



- 2.4** **Determine** the pK_a of the HX contained in the sample and **select** which one of the three acids was contained in your sample. 1.5 pt

SOLUTION:

$$pK_a = 4.25$$

☐ HA ☒ HB ☐ HC

The pK_a can be read off at the half-equivalence point. Here, $[HX] = [X^-]$. With the buffer equation $pH = pK_a + \log([X^-]/[HX])$, inserting 1 for the ratio (half-equivalence point, $[X^-] = [HX]$), we get $pH = pK_a$.

1.0 pts for the correct pK_a within ± 0.2 .

0.5 pts for choosing the acid that best fits their determined pK_a . No points awarded for checking no/multiple boxes.

Ranges: $4.790 < HA < 4.505$; $HB < 4.505$; $HC > 4.790$.

1.5 pts total.

- 2.5** **Calculate** the mass m_{HX} in g of the unknown acid HX contained in your titrated sample. **Note:** If you could not determine what acid is contained in the sample in **2.4**, assume that $M'_{HX} = 100 \text{ g mol}^{-1}$. 1.5 pt

SOLUTION:

As all acids are monoprotic, at the equivalence point ($V_{eq} = 17.5 \text{ mL}$) the following holds:

$$n_{NaOH} = n_{HX}$$

We can calculate n_{NaOH} from V_{eq} and c_{NaOH} :

$$V_{eq} \cdot c_{NaOH} = n_{NaOH} = n_{HX}$$

$$n_{HX} = 1.75 \text{ mmol.}$$

From this, we can very easily get the mass of HX in our sample:

$$m_{HX} = n_{HX} \cdot M_{HX}$$

The molecular weights of the acids HA, HB and HC are 60 g mol^{-1} , 72 g mol^{-1} and 88 g mol^{-1} , respectively. Calculating the masses for each acid would give:

$$m_{HA} = 0.105 \text{ g}$$

$$m_{HB} = 0.126 \text{ g}$$

$$m_{HC} = 0.154 \text{ g}$$

$$m'_{HX} = 0.175 \text{ g (if they used } M'_{HX} = 100 \text{ g mol}^{-1}\text{)}.$$

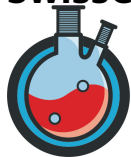
1.0 pts for the correct equation leading to n_{HX} , even if their value of V_{eq} is wrong. Keep this in mind for future calculations.

0.5 pts for the correct numerical result (plugging in M_{HX}), according to their choice of acid in **2.4**.

0.5 pts/0.5 pts are still awarded if their result of n_{HX} was incorrect, but they used the correct value of M_{HX} to determine the mass.

1.5 pts total.

You find a different sample in your laboratory cabinet. It is a solution of HA with HY (either HB or HC). You measure the ratio $\frac{[HA]}{[A]} = 0.91$. From your measurements, you can also tell that HY appears more in its protonated than in its deprotonated form.



2.6 Determine if **HY** is either **HB** or **HC**. Explain your answer.

3.0 pt

SOLUTION:

☐ **HB** ☒ **HC**

HY must be **HC**. With $[A^-]$ slightly dominating over $[HA]$, we are just above $pH = 4.76$ (4.80, as determined by $pH = pK_a - \log([HA]/[A^-])$). At this pH , only butyric acid is still mostly protonated $[HC]/[C^-] = 1.05$.

Note that no calculations are necessary for this exercise. By seeing that we are at a $pH > pK_a(HA)$, we can immediately rule out that the stronger acid **HB** would be mostly protonated, leaving only **HC**. And indeed, when checking (see above), the ratio comes out to be $[HC]/[C^-] = 1.05$, meaning **HY (HC)** is mostly protonated.

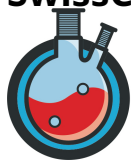
1.0 pts for the correct choice of **HY**.

2.0 pts for a sound argumentation (calculation, intuition...).

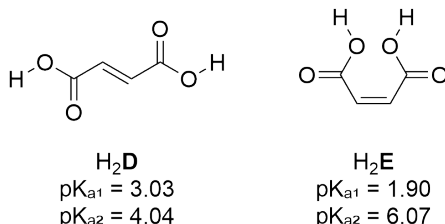
No points are awarded for choosing the correct answer without explanation.

In case of incorrect ordering in **2.2**, check if the argumentation is sound but the (wrong) result to this exercise is consistent with the result from **2.2**.

3.0 pts total.

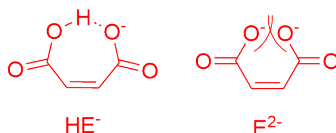


Lastly, let us consider two acids that taste fruity, tart and sweet: Fumaric acid H_2D and maleic acid H_2E . These two isomers only differ in the configuration of the central double bond, with H_2D being *trans*-configured, whereas H_2E is *cis*-configured. The differences in their pK_a values are remarkable. H_2D has pK_a values that are similar to other carboxylic acids. H_2E on the other hand, has a $\text{pK}_{a1} = 1.90$, which is significantly lower than most carboxylic acids. Its second $\text{pK}_{a2} = 6.07$ is significantly higher than expected.



- 2.7** **Explain** these findings for H_2E by considering the structure of the singly and doubly charged species HE^- and E^{2-} and listing stabilising and destabilising factors. 4.0 pt

SOLUTION:



Having a lower pK_a means being a stronger acid. Maleic acid is therefore way stronger than other carboxylic acids. This means that the conjugate base is stabilised. This stabilisation can be seen as hydrogen bonding in HE^- , that lowers the energy of the product.

The second pK_a is higher, which means the acid is weaker than usual. The product of the reaction must therefore be destabilised in some fashion. The doubly deprotonated malate has two carboxylate groups pointing directly at each other. Although every oxygen atom only carries roughly half a negative charge (many resonance forms exist), this charge-buildup leads to significant repulsion, giving a destabilised conjugate base.

0.5 pts for each correctly drawn structure (regardless of repulsion and H-bonding).

1.0 pts for some mention of the fact that lower pK_a s mean stronger acids and/or higher means weaker.

1.0 pts for the realisation that hydrogen bonding can enhance acidity.

1.0 pts for noticing that malate is destabilised by repulsion.

If other, sensible explanations are given, a total of 1.0/2.0 pts for argumentation can be awarded.

4.0 pts total.



Redox Chemistry with KMnO_4

(13.5 pts, 11%)

As an aspiring scientist, you step into the lab and notice a vibrant purple solution — potassium permanganate (KMnO_4). Curious of its oxidizing potential, you conduct some experiments.

Half Reaction	Standard Reduction Potential (E°/V)
$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	1.50
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.49
$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	1.36
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{Pt}^{2+} + 2\text{e}^- \longrightarrow \text{Pt}$	1.22
$2\text{IO}_3^- + 12\text{H}^+ + 10\text{e}^- \longrightarrow \text{I}_2 + 6\text{H}_2\text{O}$	1.21
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	0.80
$\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$	-1.18

3.1 **Provide** the oxidation state of the underlined Mn atom in the following compounds: 3.5 pt

SOLUTION:

$\text{K}_2\underline{\text{Mn}}\text{O}_4$ +VI

$\underline{\text{Mn}}_2\text{O}_7$ +VII

$\underline{\text{Mn}}\text{SO}_4$ +II

$(\text{H}_3\text{O})_2\underline{\text{Mn}}(\text{MnO}_4)_6$ +IV

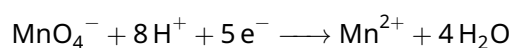
$\underline{\text{Mn}}_2(\text{CO})_{10}$ 0

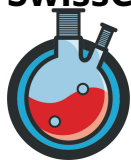
0.5 pts for each of the top three.

1.0 pts for each of the bottom two.

3.5 pts total.

Potassium permanganate's redox behaviour depends on the pH. In an acidic medium, it reacts as follows:





3.2 **Balance** the reduction of MnO_4^- in basic medium:

1.0 pt



SOLUTION:



1.0 pts for a properly balanced equation.

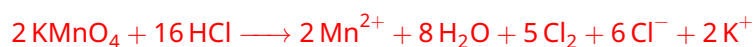
1.0 pts total.

Because you are a responsible chemist, you have read the safety instructions, so you know what happens when you mix concentrated hydrochloric acid with KMnO_4 .

3.3 **Give** the balanced reaction between KMnO_4 and hydrochloric acid.

2.0 pt

SOLUTION:



2.0 pts for any fully correctly balanced equation like the ones above.

1.0 pts for reducing Mn^{7+} to Mn^{2+} and oxidizing Cl^- to Cl_2 , even if the reaction is wrongly balanced.

1.0pts for any correctly balanced chloride complexes like $\text{K}_3[\text{MnCl}_6]$.

2.0 pts total.

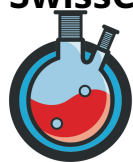
3.4 **Name** the produced molecule and **explain** why it is more dangerous than KMnO_4 .

1.0 pt

SOLUTION:

Produced molecule: chlorine/chlorine gas (Cl_2)

Explanation: Chlorine is a highly toxic **gas**. Potassium permanganate is toxic as well, but as a solid.



3.5 Select for the following solids if they react with KMnO_4 in an acidic solution and under standard condition. 1.5 pt

SOLUTION:

Au

☐ Reaction

☒ No reaction

Pt^{2+}

☐ Reaction

☒ No reaction

Ag

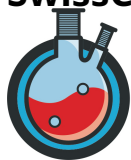
☒ Reaction

☐ No reaction

0.5 pts for each correctly assigned box.

-0.5 pts for each incorrectly assigned box (min 0.0 pts).

1.5 pts total.



In the following, we want to find out what happens to the reduction potential, if we change the pH value and the concentration of KMnO_4 . For this, you will need the Nernst equation for a half-cell:

$$E = E^\circ - \frac{RT}{zF} \cdot \ln(Q)$$

3.6 **Provide** the reaction quotient Q for the reduction of KMnO_4 in acidic medium. 0.5 pt

Note: Because the reaction happens in water, $[\text{H}_2\text{O}] = 1$.

SOLUTION:

Inserting into the formula given in the instructions, we get

$$Q = \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

0.5 pts.

0.5 pts total.

You have some KMnO_4 solution **A** with unknown ratio of Mn^{2+} and MnO_4^- ions. You put a few drops of solution **A** onto Pt, but nothing happens. Then you add some I_2 into the solution **A**, and you see that a reaction takes place. The experiments were conducted at $T = 25^\circ\text{C}$.

3.7 **Calculate** the ratio $\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]}$ at pH = 3 of solution **A** using the Nernst equation. 4.0 pt

SOLUTION:

$$\Delta E - \Delta E^\circ = -\frac{RT}{zF} \cdot \ln(Q) = 1.21\text{ V} - 1.49\text{ V}$$

We know from the pH, that $[\text{H}^+] = 1 \times 10^{-3}$. Furthermore, $z = 5$.

From the Nernst equation, we can derive

$$\exp\left(\frac{(E - E^\circ) \cdot zF}{RT}\right) \cdot [\text{H}^+]^8 = \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]} = \exp\left(\frac{0.28\text{ V} \cdot 5 \cdot 96485\text{ C mol}^{-1}}{8.314\text{ J mol}^{-1}\text{ K}^{-1} \cdot 298.15\text{ K}}\right) = \exp(54.49)$$

Inserting everything, we obtain:

$$\exp(54.49) \cdot (1 \times 10^{-3})^8 = 0.4635$$

Therefore,

$$\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]} = 0.46$$

1.0 pts for using $E - E^\circ$ correctly.

0.5 pts for $z = 5$.

0.5 pts for $[\text{H}^+] = 1 \times 10^{-3}$.

1.0 pts for an expression of $\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]}$ in terms of the Nernst equation.

1.0 pts for the correct numerical result.

4.0 pts total.



Iodine: Quiet or Explosive

(17.0 pts, 13%)

Iodine is a vital trace element with significant biological, chemical, and industrial importance, discovered in 1811 by French chemist Bernard Courtois. It is most commonly recognized for its role in human health, particularly in the synthesis of thyroid hormones, which regulate metabolism, growth, and development.



4.1 Identify the most stable oxidation state of iodine.

2.0 pt

SOLUTION:

The most stable oxidation state is -1.

Write the electron configuration for iodine both in its elementary state and in its most stable oxidation state.

SOLUTION:



Explain why this oxidation state is considered the most stable one.

SOLUTION:

With oxidation state -1, iodine reaches the electron configuration of Xe, a noble gas.

0.5 pts for correct oxidation state -I.

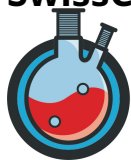
0.5 pts for each correct electron configuration.

0.5 pts/1.0 pts for giving the oxidation state +VII and the consistent electron configuration $[\text{Kr}]4d^{10}$.

0.5 pts for correct reasoning.

2.0 pts total.

There are two beakers with liquid in front of you. One contains water, the other cyclohexane. To identify them, you added some iodine to each beaker.



4.2 **Predict** the colour of each solution after adding iodine. 3.0 pt

SOLUTION:

In water: (pale) yellow/orange/brown In cyclohexane: purple

State, whether iodine be well dissolved in both solvents.

SOLUTION:

Iodine dissolves well in water.

☐ True

☒ False

Iodine dissolves well in cyclohexane.

☒ True

☐ False

Explain your thinking.

SOLUTION:

I_2 is apolar. It dissolves well in apolar solvents like cyclohexane. In polar solvents like water, it barely dissolves.

0.5 pts for each correct colour.

0.5 pts for each correct assignment of True/False.

0.0 pts for unclear/multiple choices.

1.0 pts for correct/sensible explanation.

3.0 pts total.

You take a new beaker with 100 mL water. 0.254 g I_2 and 0.166 g KI are now added to the beaker. **Note:** I_2 and I^- combine to give the triiodide anion I_3^- .

4.3 **Predict** if you will get a clear liquid phase without precipitation and **explain** your reasoning. 2.0 pt

SOLUTION:

The phase will be clear.

☒ True

☐ False

Explanation:

SOLUTION:

Each of the reagents is added in 1 mmol. The resulting triiodide anion is well-solvated in an aqueous phase. We expect to get a clear solution.

1.0 pts for the correct choice.

1.0 pts for sensible reasoning.

0.0 pts/2.0 pts for choosing an answer without any reasoning.

2.0 pts total.



- 4.4** **Draw** the three-dimensional geometric structure of I_3^- clearly, including all electron pairs. 1.0 pt

SOLUTION:

Image after discussion (electrons)



0.5 pts for correct geometry.

0.5 pts for correct electron pairs.

1.0 pts total

Iodine can form a variety of interesting and useful compounds due to its versatile chemical behaviour. An explosive example is NI_3 .

- 4.5** **Draw** the three-dimensional geometric structure of NI_3 clearly, including all electron pairs. 1.0 pt

SOLUTION:



0.5 pts for correct geometry.

0.5 pts for correct electron pairs.

1.0 pts total



Reaction/Name	Value
$\text{N}_2(\text{s}) \longrightarrow \text{N}_2(\text{l})$	$\Delta_{\text{fus}}H^\circ(\text{N}_2) = 0.7 \text{ kJ mol}^{-1}$
$\text{N}_2(\text{l}) \longrightarrow \text{N}_2(\text{g})$	$\Delta_{\text{vap}}H^\circ(\text{N}_2) = 5.6 \text{ kJ mol}^{-1}$
$\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{l})$	$\Delta_{\text{fus}}H^\circ(\text{I}_2) = 15.6 \text{ kJ mol}^{-1}$
$\text{I}_2(\text{l}) \longrightarrow \text{I}_2(\text{g})$	$\Delta_{\text{vap}}H^\circ(\text{I}_2) = 41.8 \text{ kJ mol}^{-1}$
$\text{N}(\text{g}) \longrightarrow \text{N}(\text{g})^+ + \text{e}^-$	$\text{IE}(\text{N}) = 1402.3 \text{ kJ mol}^{-1}$
$\text{N}(\text{g}) + \text{e}^- \longrightarrow \text{N}^-(\text{g})$	$\text{EA}(\text{N}) = -6.8 \text{ kJ mol}^{-1}$
$\text{I}(\text{g}) \longrightarrow \text{I}^+(\text{g}) + \text{e}^-$	$\text{IE}(\text{I}) = 1008.4 \text{ kJ mol}^{-1}$
$\text{I}(\text{g}) + \text{e}^- \longrightarrow \text{I}^-(\text{g})$	$\text{EA}(\text{I}) = 295.0 \text{ kJ mol}^{-1}$
$\text{N}_2(\text{g}) \longrightarrow 2 \text{N}(\text{g})$	$\text{BDE}(\text{N}_2) = 945 \text{ kJ mol}^{-1}$
$\text{I}_2(\text{g}) \longrightarrow 2 \text{I}(\text{g})$	$\text{BDE}(\text{I}_2) = 151 \text{ kJ mol}^{-1}$
$\text{NI}_3(\text{g}) \longrightarrow \text{N}(\text{g}) + 3 \text{I}(\text{g})$	$\text{BDE}(\text{NI}_3) = 169 \text{ kJ mol}^{-1}$ (per bond)
Standard molar entropy of $\text{N}_2(\text{g})$	$\Delta S^\circ(\text{N}_2(\text{g})) = 191.6 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard molar entropy of $\text{I}_2(\text{s})$	$\Delta S^\circ(\text{I}_2(\text{s})) = 260.7 \text{ J mol}^{-1} \text{ K}^{-1}$
Standard molar entropy of $\text{NI}_3(\text{g})$	$\Delta S^\circ(\text{NI}_3(\text{g})) = 344.3 \text{ J mol}^{-1} \text{ K}^{-1}$

This table includes entries for various thermodynamic quantities concerning nitrogen, iodine and nitrogen triiodide.

- 4.6** Based on the data and reactions in the table, **determine** the molar formation enthalpy $\Delta_f H^\circ$ of gaseous NI_3 from $\text{I}_2(\text{s})$ and $\text{N}_2(\text{g})$ in kJ mol^{-1} . 4.0 pt

SOLUTION:



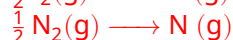
$$\frac{3}{2} \Delta_{\text{fus}}H^\circ(\text{I}_2) = 23.3 \text{ kJ mol}^{-1}$$



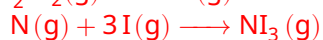
$$\frac{3}{2} \Delta_{\text{vap}}H^\circ(\text{I}_2) = 62.7 \text{ kJ mol}^{-1}$$



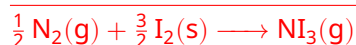
$$\frac{3}{2} \text{BDE}(\text{I}_2) = 226.5 \text{ kJ mol}^{-1}$$



$$\frac{1}{2} \text{BDE}(\text{N}_2) = 472.5 \text{ kJ mol}^{-1}$$



$$-3 \text{BDE}(\text{NI}_3) = -507.0 \text{ kJ mol}^{-1}$$

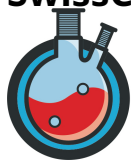


$$\Delta_f H^\circ(\text{NI}_3) = 278.0 \text{ kJ mol}^{-1}$$

0.5 pts for each correctly used equation.

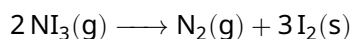
1.5 pts for the correct numerical result.

4.0 pts total.



4.7 **Show** that the explosion reaction of nitrogen triiodide:

4.0 pt



is spontaneous at $T = 298 \text{ K}$. **Note:** If you could not calculate $\Delta_f H^\circ(\text{NI}_3(\text{g}))$ in 4.6, use $\Delta_f H^\circ(\text{NI}_3(\text{g}))' = 300 \text{ kJ mol}^{-1}$ instead.

SOLUTION:

For the reaction: $2 \text{NI}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3 \text{I}_2(\text{s})$

$$\Delta_r H^\circ = \Delta_f H^\circ(\text{N}_2(\text{g})) + 3\Delta_f H^\circ(\text{I}_2(\text{s})) - 2\Delta_f H^\circ(\text{NI}_3(\text{g})) = -2\Delta_f H^\circ(\text{NI}_3(\text{g})) = -556 \text{ kJ mol}^{-1}$$

(With the value in the hint: -600 kJ mol^{-1} .)

$$\Delta_r S^\circ = \Delta_S^\circ(\text{N}_2(\text{g})) + 3\Delta_S^\circ(\text{I}_2(\text{s})) - 2\Delta_S^\circ(\text{NI}_3(\text{g})) = 285.1 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r G = \Delta_r H - T\Delta_r S = -640.96 \text{ kJ mol}^{-1} \text{ (With the value in the hint: } -684.96 \text{ kJ mol}^{-1}.)$$

The reaction is spontaneous, because $\Delta_r G < 0$.

Mark the correct driving force(s) for the reaction.

- ☐ enthalpy-driven
- ☐ entropy-driven
- ☐ both of the above
- ☐ none of the above

SOLUTION:

- ☐ enthalpy-driven
- ☐ entropy-driven
- ☒ both of the above
- ☐ none of the above

0.5 pts for the correct formula for enthalpy.

0.5 pts for the correct numerical value of enthalpy.

0.5 pts for the correct formula for entropy.

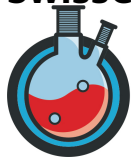
0.5 pts for the correct numerical value of entropy.

0.5 pts for the correct formula for free energy.

0.5 pts for the correct numerical value of free energy.

1.0 pts for the correctly assigned driving force(s), as long as consistent with their calculations above.

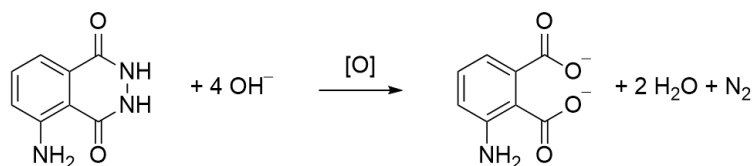
4.0 pts total.



Luminol Literally Lighting Labs

(11.0 pts, 13%)

Let's consider the following reaction:

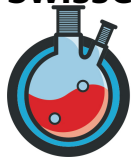


In this reaction, luminol is oxidised to a 3-aminophthalate dianion. Under ideal conditions, the quantum yield of the reaction is approximately 0.01 so each molecule of luminol that reacts and enters an excited state has a $p = 1\%$ chance that a photon will be emitted. The wavelength of the emitted photon is $\lambda = 425 \text{ nm}$. We assume that the energy released in this oxidation of one molecule of luminol is either all lost as light or all lost as heat.

For the following exercise, we will be working with a reactor that allows us to control exactly how many moles of luminol are *reacting* inside the reactor per second. To achieve this, all reactants except for luminol (coming from **A**) are kept in large excess and luminol is gradually added to the reactor to keep the rate (mol s^{-1}) at which luminol is reacting constant. The products then flow into **B**.



We start our reactor and place solar cells all around the reactor to capture all the photons that are emitted. We measure that our solar cells are continually converting $P = 0.1 \text{ W}$ of light into electricity. We assume the efficiency of the solar cells is 100% and that they are insensitive to infrared light.



- 5.1** **Calculate** the reaction enthalpy $\Delta_r H$ in kJ mol^{-1} and the rate r_1 in mol s^{-1} at which luminol is consumed in this reaction. 4.0 pt

SOLUTION:

Energy per photon: $E = \frac{hc}{\lambda} = 4.68 \times 10^{-19} \text{ J}$

$\Delta_r H = -E \times N_A = -\frac{h \times c \times N_A}{\lambda} = -282 \text{ kJ mol}^{-1}$

$r_1 = -\frac{P}{p \times \Delta_r H} = -\frac{P \times \lambda}{p \times h \times c \times N_A} = 3.6 \times 10^{-5} \text{ mol s}^{-1}$

0.5 pts for energy per photon formula.

0.5 pts for the energy of a photon (numerical).

0.5 pts each for the formula of the reaction enthalpy and the rate of reaction.

1.0 pts each for the numerical results/calculation of the reaction enthalpy and the rate of reaction.

4.0 pts total.

Our lab experiences a power outage that does not affect our reactor. We want to replace the light bulb at the ceiling with our reactor (emits the same number of photons). The light bulb has an efficiency $\eta = 10\%$, emits light at $\lambda = 589 \text{ nm}$ and runs on a power $P = 60 \text{ W}$.

- 5.2** **Calculate** the reaction rate r_2 in mol s^{-1} we need to replace the light bulb. 4.0 pt

SOLUTION:

Emission rate of light bulb: $S = \frac{P \times \eta \times \lambda}{h \times c} = 1.8 \times 10^{18} \text{ s}^{-1}$

Emission rate of reactor: $r_2 \times N_A \times p$

Rate needed to replace bulb: $r_2 \times N_A \times p \stackrel{!}{=} \frac{P \times \eta \times \lambda}{h \times c} = S$

$r_2 = \frac{P \times \eta \times \lambda}{h \times c \times N_A \times p} = 3 \times 10^{-3} \text{ mol s}^{-1}$

1.0 pts for the formula of the emission rate of the light bulb.

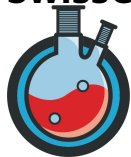
1.0 pts for the formula of the emission rate of the reactor.

1.0 pts for correct usage of the formulae (setting them equal, transformation) or the correct thinking of how to solve (could be calculations).

1.0 pts for the numerical result.

4.0 pts total.

Now we switch off our reactor. After 15 seconds, we measure the rate of emitted photons to be $\frac{N_{15}}{N_0} = 0.333$, where N_{15} is the rate measured after 15 s and N_0 is the rate measured while running the reactor at the conditions of task 5.2. **Hint:** With all other reagents in vast excess, the reaction becomes first order in luminol concentration.



5.3 Calculate the value of $\frac{N_{42}}{N_0}$ at $t = 42$ s after switching off the reactor.

3.0 pt

SOLUTION:

First order reaction $\rightarrow A(t) = A_0 \times e^{-kt}$

Because $N \propto A$: $N_t = N_0 \times e^{kt}$

$$k = -\frac{\ln\left(\frac{N_{15}}{N_0}\right)}{t} = 0.0732\text{s}^{-1}$$

$$\frac{N_{42}}{N_0} = e^{kt} = 0.046$$

1.0 pts for the realisation it's 1st order and/or the formula.

1.0 pts for reasoning/formula/sensible calculations.

1.0 pts for the numerical result.

3.0 pts total.

5.4 List four reasons why illuminating your lab with a luminol reactor is a terrible idea.

2.0 pt

SOLUTION:

Some possible answers:

Too expensive

Only 1% of the energy is emitted as light, so huge amounts of heat to handle

Eyes have low sensitivity in that range

Dangerous to handle huge amounts of oxidiser

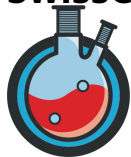
Setup too bulky

Too complicated

Waste disposal

0.5 pts per sensible answer (also ones not included here).

2.0 pts total.



Carbon Clock: Archeology and *in vivo* Imaging (16.0 pts, 15%)

Radiocarbon dating uses the ^{14}C isotope to estimate the age of carbon-bearing material. This radioactive carbon isotope decays into ^{14}N .

6.1 **Choose** the particle emitted upon radioactive decay of ^{14}C .

1.0 pt

SOLUTION:

☐ α

☐ β^+

☒ β^-

By going from ^{14}C to ^{14}N , a proton needs to be created. From the three processes, only β^- converts a neutron into a proton.

1.0 pts for correct answer.

0.0 pts for multiple/unclear answer.

1.0 pts total.

6.2 **Give** the kinetic order of radioactive decay.

1.0 pt

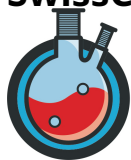
SOLUTION:

Because the rate of decay is proportional to the number of radio nuclei, the order is 1.

1.0 pts for the correct order.

1.0 pts total.

The use of ^{14}C isotope for archaeological age determination was proposed by Libby in 1949. For this purpose, however, the half-life of ^{14}C first needed to be determined. Libby found that a contemporary tree sample emits around 12.5 particles per minute per gram of carbon. For his research, he also measured the activity of one archaeological sample, which was 2928 years old at the time, and found that it emitted only 8.78 particles per minute per gram of carbon.



6.3 Determine the rate constant k in year^{-1} for the decay of ^{14}C .

2.5 pt

Assumptions:

- The level of ^{14}C in the atmosphere remains constant over time due to continuous synthesis in the upper atmosphere.
- Living organisms actively exchange carbon with their surroundings and maintain a constant ^{14}C -level.

SOLUTION:

$\ln\left(\frac{N_0}{N_1}\right) = k(t_1 - t_0)$, as activity is proportional to number of atoms/concentration:

$\ln\left(\frac{r_0}{r_1}\right) = k(t_1 - t_0)$, where r_i is the rate of emission at time i . From this we get $k = 1.21 \times 10^{-4} \text{ year}^{-1}$.

1.0 pts for understanding the proportionality of activity and concentration.

1.0 pts for applying first-order kinetics.

0.5 pts for correct numerical result.

2.5 pts total.

6.4 Determine the half-life of ^{14}C in years. **Note:** If you could not determine k in 6.3, use $k' = 1.00 \times 10^{-4} \text{ year}^{-1}$ instead.

1.5 pt

SOLUTION:

$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$, therefore $t_{\frac{1}{2}} = 5745 \text{ years}$.

If they used k' instead, $t_{\frac{1}{2}} = 6932 \text{ years}$.

1.0 pts for the correct use of the formula.

0.5 pts for the correct numerical result.

1.5 pts total.

6.5 Propose two coordinates, $f(r)$ and $g(t)$, such that any data obtained about the ^{14}C emission rate r and age t will plot as a single straight line.

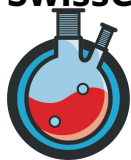
1.0 pt

SOLUTION:

By using $f(r) = \ln(r)$ and $g(t) = t$ (unchanged), we will linearise the exponential decay.

1.0 pts for both correct transformations.

1.0 pts total.



- 6.6** Determine the natural level of ^{14}C in contemporary carbon in parts per trillion (ppt). Hint: $1 \text{ ppt} = \frac{1 \text{ g}}{1 \times 10^{12} \text{ g}}$. 2.5 pt

SOLUTION:

From $A = kN$, we can derive that $r = k \cdot w(^{14}\text{C})$. Before using this formula, it is important to convert all numbers to the same units.

$$k = 1.21 \times 10^{-4} \text{ year}^{-1} = 2.30 \times 10^{-10} \text{ min}^{-1}$$

$$r = 12.5 \text{ g}^{-1} \text{ min}^{-1} = 150 \text{ mol}^{-1} \text{ min}^{-1} \text{ (here it is important to use the molecular weight of natural carbon: } 12 \text{ g mol}^{-1}, \text{ not } 14 \text{ g mol}^{-1} \text{!)}$$

$$N(^{14}\text{C}) = 6.52 \times 10^{11} \text{ mol}^{-1}$$

$$w(^{14}\text{C}) = N(^{14}\text{C})/Na = 1.08 \times 10^{-12} \text{ mol}^{-1} = 1.08 \text{ ppt}$$

$$w(^{14}\text{C}) = 1.31 \text{ ppt}, \text{ if using } k = 1.00 \times 10^{-4} \text{ year}^{-1}$$

Another radioactive isotope of carbon, isotope **X**, forms ^{11}B upon decay (α , β^+ , or β^-).

- 6.7** Identify the carbon isotope **X**, the decay type, and provide the corresponding nuclear reaction. 2.0 pt

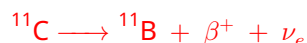
SOLUTION:

X: ^{11}C

Emitted particle: ☐ α

☒ β^+

☐ β^-



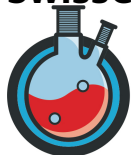
0.5 pts for the correct isotope.

0.5 pts for the correct emission.

1.0 pts for the correct decay reaction.

0.5 pts/1.0 pts for the correct decay reaction, missing the neutrino.

2.0 pts total.



Isotope **X** is used in drug discovery and medicine for *in vivo* imaging. The binary compound **A** ($w(\text{O}) = 74.37\%$), which contains isotope **X**, is obtained directly from a cyclotron. Compound **A**, upon reduction with LiAlH_4 without quenching, yields compound **B** ($w(\text{O}) = 43.27\%$). A subsequent reaction with HI then produces compound **C** ($w(\text{I}) = 90.08\%$). Compound **C** is a key intermediate that can be used in nucleophilic substitution reactions to rapidly introduce isotope **X** into organic molecules. Notably, each of these chemical steps requires just 5 minutes. Chemical steps are automated and one happens immediately after the other.

6.8 Identify A, B, and C. Providing calculations is optional.

3.0 pt

SOLUTION:

A: $^{11}\text{CO}_2$

B: $^{11}\text{CH}_3\text{OLi}$

C: $^{11}\text{CH}_3\text{I}$

1.0 pts for each correct sum formula.

3.0 pts total.

Typical activity of compound **A**, as obtained from cyclotron, is 300 MBq.

6.9 Calculate the activity A_{C} of the obtained sample of compound **C** (in MBq) immediately after the second step, assuming all synthesis steps are quantitative (100% yield). The half-life of isotope **X** is 20 minutes.

1.5 pt

SOLUTION:

The total reaction time is 10 min. So only half of the half-life has passed. This means that the activity has decreased by a factor of $\sqrt{2}$. Because the activity is proportional ($A = kN$), the new activity must now be

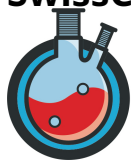
$$A_{\text{C}} = \frac{300 \text{ MBq}}{\sqrt{2}} = 212 \text{ MBq.}$$

0.5 pts for calculating the total time of the reactions.

0.5 pts for any correct calculation of the number of radioactive particles or reasoning by how much it has decreased.

0.5 pts for the correct numerical value of A_{C} .

1.5 pts total.



Gaslighting and Lighting Gasses

(12.5 pts, 11%)

You find two gas cylinders in an old, dusty corner of your laboratory, neither of which are labelled with their contents. You are, however, sure, that both of them contain a single type of molecule. One of the cylinders contains substance **A**, whereas the other contains substance **B**.

In order to pass the next safety inspection, we must now figure out what the contents of the cylinder are and label them accordingly! First, we will gain some insight using density and masses. Then, we shall explore some reactions and try to light them on fire!

You fill gas **A** into a balloon. Once filled, the radius of the balloon measures $r = 12$ cm.

- 7.1** **Calculate** the volume V_{balloon} in L filled with **A**, assuming the balloon to be a sphere. 1.0 pt

SOLUTION:

The volume of a sphere is $V = \frac{4\pi}{3} \cdot r^3$.

Inserting $r = 12$ cm, we very easily obtain $V_{\text{balloon}} = 7.24$ L.

0.5 pts for the correct use of the volume of a sphere.

0.5 pts for the correct numerical result.

1.0 pts total.

With some tricks, you determine the mass of the filled balloon to be $m_{\text{balloon+A}} = 14.203$ g under ambient conditions ($p = 1 \times 10^5$ Pa, $T = 25$ °C). Under the same conditions, a balloon inflated to the same radius with air, reads $m_{\text{balloon+air}} = 9.773$ g. Air is a composition of 79% N_2 and 21% O_2 by mass.

- 7.2** **Calculate** the mass of the empty balloon m_{balloon} in g. **Note:** If you could not calculate V_{balloon} in **7.1**, use $V'_{\text{balloon}} = 7.50$ L instead. 2.5 pt

SOLUTION:

For this, we can use the control experiment ran with air. Using the ideal gas law, we know that

$$n_{\text{air}} = \frac{pV}{RT} = 0.292 \text{ mol}$$

Using the composition of air, we get:

$$M_{\text{air}} = 0.79 \cdot 28 \text{ g mol}^{-1} + 0.21 \cdot 32 \text{ g mol}^{-1} = 28.84 \text{ g mol}^{-1}$$

We can now calculate the mass of air contained inside the balloon.

$$m_{\text{air}} = M_{\text{air}} \cdot n_{\text{air}} = 8.421 \text{ g.}$$

Subtracting the mass of air from the total mass of the filled balloon, we obtain

$$m_{\text{balloon}} = m_{\text{balloon+air}} - m_{\text{air}} = 9.773 \text{ g} - 8.421 \text{ g} = 1.352 \text{ g.}$$

Note: No matter what the volume of V_{balloon} they used, they should obtain the same result.

1.0 pts for using the ideal gas law to obtain n_{air} .

1.0 pts for mathematically sound way of getting to m_{air} .

0.5 pts for the correct numerical result of m_{balloon} .

2.5 pts total.



7.3 **Calculate** the molar mass $M_{\mathbf{A}}$ of molecule **A** in g mol^{-1} . **Note:** If you could not calculate m_{balloon} in 7.2, use $m'_{\text{balloon}} = 1.40 \text{ g}$ instead. 2.0 pt

SOLUTION:

The total mass $m_{\text{balloon}+\mathbf{A}} = m_{\text{balloon}} + m_{\mathbf{A}}$.

Because both air and **A** are assumed to behave like ideal gasses, we know that the same volume will give the same number of particles. Therefore, as the radius of the balloon is the same in both cases,

$$n_{\text{air}} = n_{\mathbf{A}} = 0.292 \text{ mol.}$$

The mass of **A** is calculated easily:

$$m_{\mathbf{A}} = m_{\text{balloon}+\mathbf{A}} - m_{\text{balloon}} = 12.851 \text{ g (12.803 g if they used } m'_{\text{balloon}}).$$

Lastly,

$$M_{\mathbf{A}} = \frac{m_{\mathbf{A}}}{n_{\mathbf{A}}} = 44.0 \text{ g mol}^{-1} \text{ (43.8 g mol}^{-1} \text{ if they used } m'_{\text{balloon}}).$$

Note: No matter what the volume of V_{balloon} they used, they should obtain the same result.

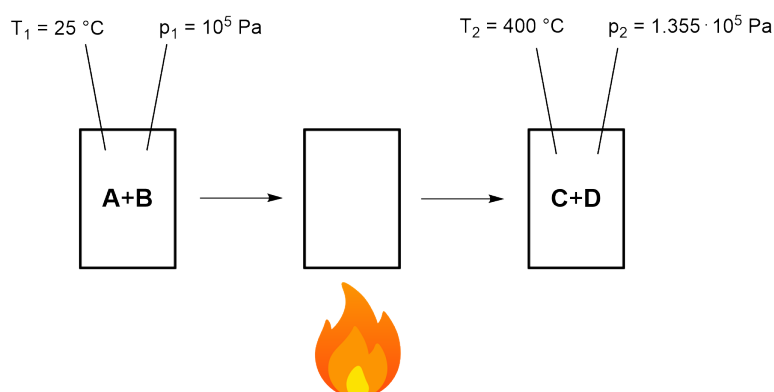
0.5 pts for getting n_{air} , either through the ideal gas law or smart thinking (from 7.2).

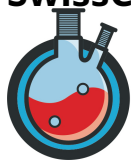
0.5 pts for a way to get to $m_{\mathbf{A}}$.

1.0 pts for the correct numerical value of $M_{\mathbf{A}}$.

2.0 pts total.

You experiment around with the gasses. Your reaction vessel with a constant volume $V_{\text{vessel}} = 5 \text{ L}$ is filled with 1 L of **A** with 4 L of **B** at $T_1 = 25^\circ\text{C}$. The mixture is then heated to $T_2 = 400^\circ\text{C}$. Once T_2 is reached, your pressure gauge shows a continuous drop in pressure at a constant temperature. Once the pressure has stabilised to $p_2 = 1.355 \times 10^5 \text{ Pa}$ at $T_2 = 400^\circ\text{C}$, you obtain a mixture of only two products, **C** and **D**.





7.4 **Explain** the reason why the pressure is dropping during this process.

1.0 pt

SOLUTION:

A reaction between **A** and **B** is occurring. As V, T stay constant, it must follow that n is decreasing, i.e. there are fewer particles on the product side than the starting materials.

1.0 pts for correct reasoning.

0.5 pts/1.0 pts for incorrect reasoning, that is formally fine (i.e. "there is a leak in the system").

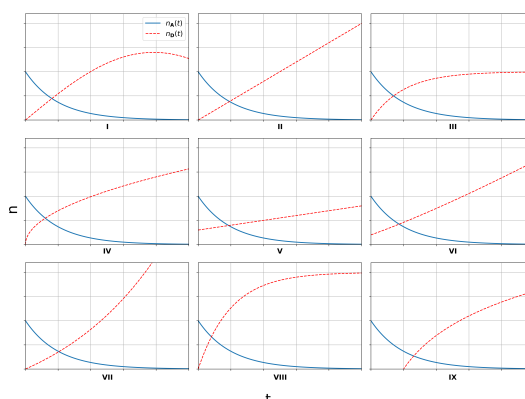
1.0 pts total.

You then cool the mixture to room temperature and open the vessel. Product **D** is obtained as a colourless liquid with density $\rho_D = 1 \text{ g mL}^{-1}$ with $m_D = 1.45 \text{ g}$.

7.5 **Circle** the graph that correctly describes the amount of **D** $n_D(t)$ over time, given the amount of **A** $n_A(t)$.

2.0 pt

SOLUTION:



Given the mass of **D**, and its other properties (density, liquid at r.t.), we can "guess"/deduce that it is water. We also obtain that

$$n_D = \frac{m_D}{M_{H_2O}} = \frac{1.45 \text{ g}}{18 \text{ g mol}^{-1}} = 0.081 \text{ mol}$$

$$n_A = \frac{p \cdot V_A}{RT} = \frac{1 \times 10^5 \text{ Pa} \cdot 1 \text{ L}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K}} = 0.040 \text{ mol}$$

we can ascertain that for every **A** consumed, two **D** are produced.

Given the set of nine possible curves, only curve **VIII** mirrors the decay of **A** and yields twice the number of particles.

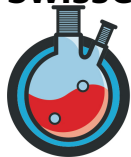
2.0 pts for selecting **VIII**.

1.0 pts/2.0 pts for selecting either **II** or **III** (either stoichiometry or curve wrong).

0.0 pts/2.0 pts otherwise.

2.0 pts total.

Lastly, you perform some experiments using fire and find the following:



- **A** extinguishes the flame.
- **B** explodes and reacts to **D**.
- **C** explodes and reacts to **A** & **D**.
- **D** extinguishes the flame.

7.6 **Assign** a chemical formula to all substances (**A**, **B**, **C** & **D**). **Balance** the reaction equation transforming **A** and **B** into **C** and **D**. 4.0 pt

SOLUTION:



The compounds can be ascertained at this point. **A** has a molar mass of 44 g mol^{-1} and extinguishes flames. Furthermore, it is also the product of a combustion. **A** is CO_2 .

B is very light and burns to only produce a single compound. By knowing that **D** is water, we know that hydrogen must come from somewhere. **B** is therefore H_2 .

C is combustible. By looking at the total pressure p_2 , we can also figure out that for each **A** consumed, only one **C** is produced. It also contains hydrogen and is a gas. **C** is therefore CH_4 .

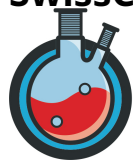
D is water, as discussed above. Its density, it being a liquid at room temperature and resulting in combustions make this very clear.

0.5 pts per correctly assigned chemical.

0.5 pts per correct stoichiometric coefficient.

Also check for alternate solutions. If they use ethane/ethylene/propane... and they get the coefficients right, subtract -0.5 pts. This does not match the information given above, but that should not be required to solve this task.

4.0 pts total.

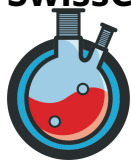


Tasting the Right (and Left) Sugars

(16.0 pts, 11%)

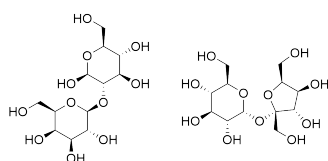
Sugars are a group of structurally related molecules consisting of polyhydroxy aldehydes or ketones. Despite their structural similarities, sugars exhibit unique properties depending on their stereochemistry and oxidation states. In this exercise, we will be looking at various types of sugars, their similarities and differences, as well as a practical way to differentiate between them in the lab.

Isomers are molecules with the same chemical formula but different connectivity or spatial arrangement of atoms. Isomers can have vastly different properties, for example, while starch, a polymer of α -glucose, is digestible by humans and fundamental for our survival, cellulose, a polymer of β -glucose, is found in cell walls and is indigestible by humans.



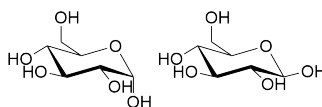
8.1 **Determine** the relationship between the following pairs of molecules by ticking the correct box. 6.0 pt

A



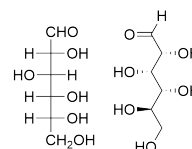
- ☐ identical
☐ enantiomers
☐ diastereomers
☐ constitutional isomers
☐ none of the above

B



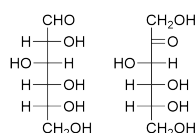
- ☐ identical
☐ enantiomers
☐ diastereomers
☐ constitutional isomers
☐ none of the above

C



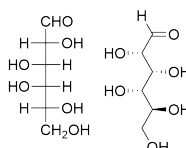
- ☐ identical
☐ enantiomers
☐ diastereomers
☐ constitutional isomers
☐ none of the above

D



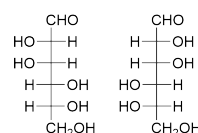
- ☐ identical
☐ enantiomers
☐ diastereomers
☐ constitutional isomers
☐ none of the above

E



- ☐ identical
☐ enantiomers
☐ diastereomers
☐ constitutional isomers
☐ none of the above

F



- ☐ identical
☐ enantiomers
☐ diastereomers
☐ constitutional isomers
☐ none of the above

SOLUTION:

A: constitutional isomers. **B:** diastereomers. **C:** identical

D: constitutional isomers. **E:** diastereomers. **F:** enantiomers

1.0 pts for each correctly assigned relationship.

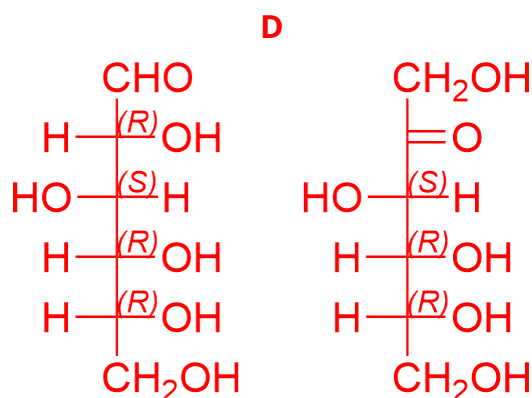
6.0 pts total.



8.2 **Circle** the stereogenic centres in the molecules from **D** and **determine** *R/S*.

2.0 pt

SOLUTION:



1.0 pts for each fully correct molecule.
2.0 pts total.

All simple sugars either contain an aldehyde or a ketone in their open form, and chemists have developed a simple test to distinguish between the two types. The reagent is prepared by mixing silver nitrate, sodium hydroxide and ammonia. In the presence of an aldehyde, silver will precipitate and form a “silver mirror” inside the glassware (positive test). In the case of a ketone, no reaction will take place, as ketones cannot be further oxidized (negative test).

8.3 **Provide** the name of this test.

1.0 pt

SOLUTION:

Tollens' test

Silver mirror test

1.0 pts for the correct name (either answer gives full points).

1.0 pts total.

8.4 **Determine** the oxidation state of Ag in $[\text{Ag}(\text{NH}_3)_2]^+$ and Ag(s).
 $[\text{Ag}(\text{NH}_3)_2]^+ \quad \underline{\hspace{2cm}}$

1.0 pt

Ag(s) $\underline{\hspace{2cm}}$

SOLUTION:

$[\text{Ag}^+(\text{NH}_3)_2]^+$

$\text{Ag}^0(\text{s})$

0.5 pts for each correct oxidation state.

1.0 pts total.



- 8.5** Write down the half-reaction and overall reaction between your sugar RCHO and the silver reagent $[\text{Ag}(\text{NH}_3)_2]^+$. 5.0 pt

SOLUTION:

Oxidation:



Reduction:



Overall reaction:



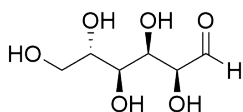
1.5 pts for each correct half-reaction.

2.0 pts for the correctly balanced overall reaction.

5.0 pts total.

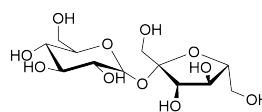
- 8.6** Mark which of the following sugars will produce a silver mirror, as described above. 1.0 pt

SOLUTION:



☒ positive test

☐ negative test



☐ positive test

☒ negative test

Aldoses (sugars with aldehydes) will produce a positive test. Sucrose will not.

0.5 pts each.

0.0 pts/0.5 pts for multiple/unclear selections.

1.0 pts total.



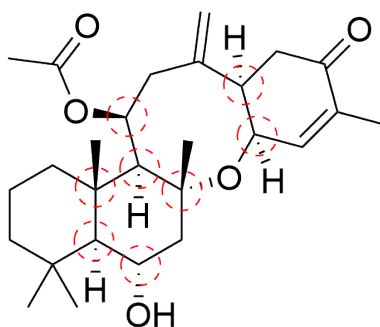
Organic Reactions

(13.0 pts, 9%)

9.1 **Circle** all the stereogenic centres in the following molecule.

4.0 pt

SOLUTION:



0.5 pts for each correctly identified stereogenic centre.

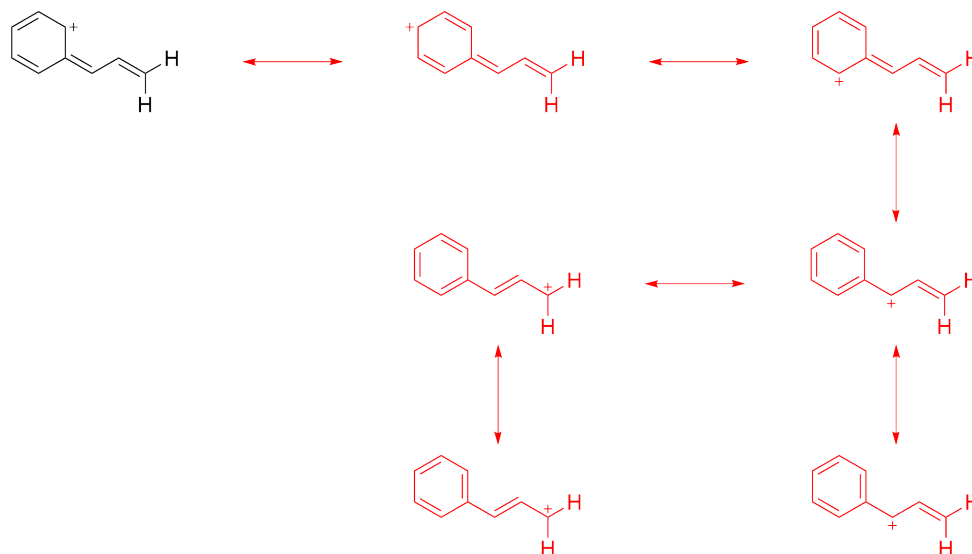
-0.5 pts for each incorrectly circled centres.

Minimum points is 0.0 pts.

4.0 pts total.

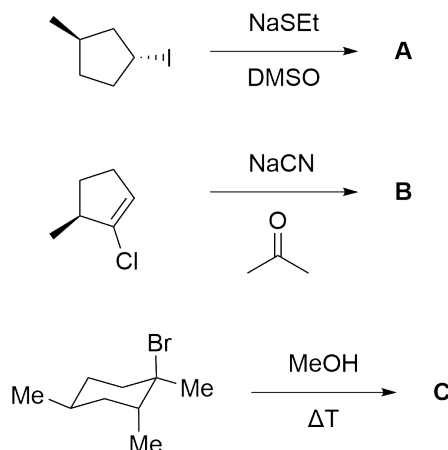
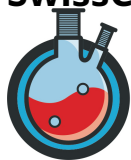
9.2 **Draw** all the resonable possible resonance structures of the carbocation below. 3.0 pt

SOLUTION:



0.5 pts for each correct resonance structure from above.

3.0 pts in total.



9.3 For the reactions provided above, **determine** which of the following reactions take place: 1.5 pt

S_N1 , S_N2 , E1, E2, $E1_{cb}$, S_NAr , no reaction

SOLUTION:

A: S_N2

B: no reaction

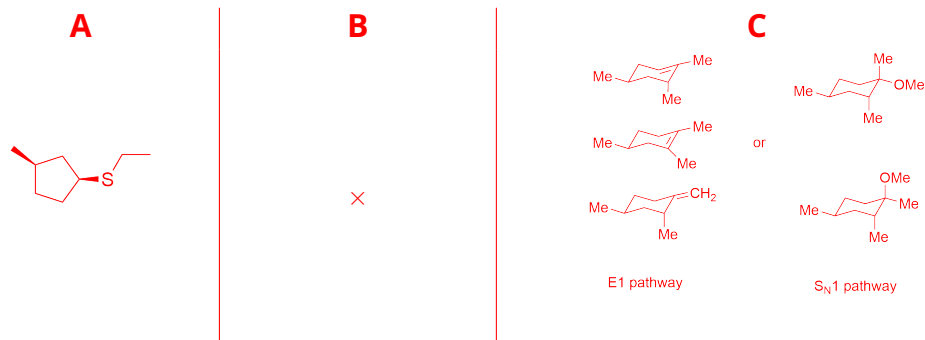
C: E1 (or S_N1)

0.5 pts each.

1.5 pts total.

9.4 **Draw** the major products **A–C**. If no reaction takes place, **place** a cross (×). 1.5 pt

SOLUTION:



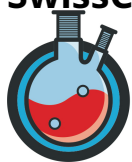
0.5 pts for each correct structure.

0.0 pts for incorrect orientation.

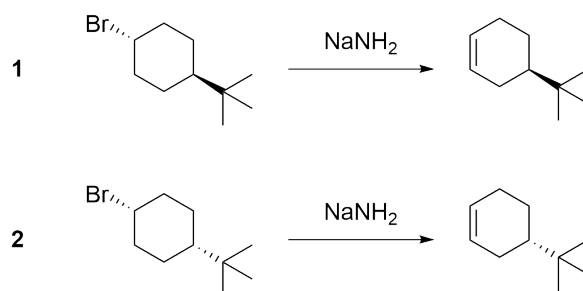
0.5 pts if S_N1 was chosen and **C** and the product is correct.

Check for mistakes in 9.3 and grade accordingly. No double-punishment.

1.5 pts total.



- 9.5 The two following eliminations (**1** & **2**) occur at different rates. Explain which of the two is faster and why using diagrams and drawings. 3.0 pt



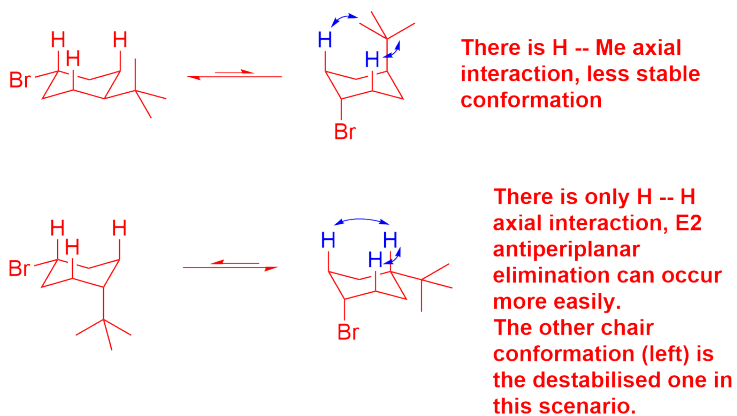
SOLUTION:

Faster reaction:

☐ **1**

☒ **2**

Explanation:



1.0 pts for correct choice of **1** or **2**.

2.0 pts for a correct explanation of the rates.

0.5 pts or 1.0 pts/2.0 pts for any reasonable but wrong explanation if **1** was chosen (e.g. mentioning anti-periplanar geometry, axial interactions, drawing ring flips, etc.).

3.0 pts total.