2013 UNIT 3/4 EXAM SOLUTIONS

Penalties : the usual ones!
* max^m 1 mark off if incorrect numbers of significant figures are given
* max^m 1 mark off if symbols of state are omitted
* 1 mark off each time a unit is omitted from answer that requires a unit

SECTION A [30 × 1 = **30**]

1. D	2. C	3. A	4. D	5. D	6. B	7. A	8. D	9. C	10. A
11. A	12. D	13. D	14. D	15. B	16. A	17. B	18. C	19. C	20. D
21. B	22. C	23. A	24. B	25. C	26. B	27. A	28. C	29. B	30. A

SECTION B [total = **95**] * = 1 mark

Question 1 (9 marks)

a) Step 3: $NH_3(g) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$ *
Or $NH_3(g) + H^+(aq) \rightarrow NH_4^+(aq)$

Step 4: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ *
Or $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

b) n(HCl) reacted with $NH_3(g)$ = n(HCl) supplied – n(HCl) in excess
= n(HCl) supplied – n(NaOH) = $0.100 \times 100\times10^{-3} - 0.200 \times 31.4\times10^{-3}$ *
= 0.0100 – 0.00628
= 0.00372 mol * (3 sig fig)

c) n(N) in sample = $n(NH_3)$ produced = n(HCl) reacting with NH_3 = 0.00372 mol
m(N) in sample = 0.00372 x 14.0 = 0.0521 g *

d) % N = [m(N) / m(sample)] x 100 = (0.052 / 5.152) x 100
= **1.01 %** * (3 sig figs)

e) $K_a = 5.8\times10^{-10}$ - Data Book Table 12
$K_a = [B(OH)_4^-][H^+] / [H_3BO_3] = 5.8 \times 10^{-10} = [H^+]^2 / 0.647$
$[H^+]^2 = 5.8 \times10^{-10} \times 0.647$ * = $[H^+] = \sqrt{(5.8 \times10^{-10} \times 0.647)} = 1.94\times10^{-5}$ M *
pH = $-\log_{10}(1.94 \times10^{-5})$ = **4.7** * (2 sig fig)

Question 2 (8 marks)

a) The identity of each peak could be established by *running a sample of each alkanol* through the column and *noting the retention time*. *

b) 1 mark for recognising the overlap of ethanol and 2-methylpropanol peaks, that could create problems if 2-methylpropanol is in wine sample

c) retention time around 7.2.* 1-pentanol is the next alkanol in the homologous series * and the retention time seems to be increasing by a little over 1 with each member of the
- 1 mark for nominating a retention time around 7 (should be between 7 and 7.5)
- 1 mark for linking the retention time to the position of the alkanol in the homologous series

d) 1-butanol and 2-methylpropanol are structural isomers * but their retention times are quite different.* This suggests that this technique might have the potential to separate structural isomers.

e) If the concentration is doubled, the <u>area under the peak</u> (peak height is not sufficient) should be doubled.*

f) At a higher temperature, the retention times of each alkanol should be shorter.* The order of peaks will be the same.

Question 3 (9 marks)

a) (i) Mass of hydrogen = 2.800 – 1.710 – 0.664 = 0.426 g*
(ii) EF = $\frac{1.71}{12} : \frac{0.664}{14} : \frac{0.426}{1}$ = 0.142 : 0.0474 : 0.426 = 3 : 1 : 9 *

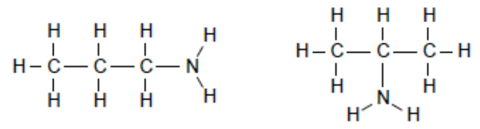
EF = C_3H_9N *

b) (i) The base peak has a value of 29 *

(ii) The parent molecular ion has a mass of 59. This matches the empirical formula of C_3H_9N. Therefore, the empirical formula and the molecular formula are both C_3H_9N.*

c)

Isomer 1 Isomer 2



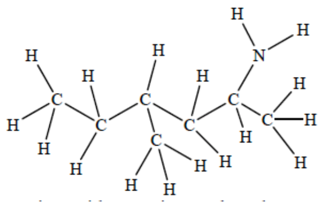
Isomer 1: 1-aminopropane (or propan-1-amine)*
Isomer 2: 2-aminopropane (or propan-2-amine)*
1 mark for each structure with its correct name.

c) The molecule is 2-aminopropane. *

It has <u>three</u> **<u>different</u>** hydrogen environments* in its structure and this matches the NMR shown. 1-aminopropane would have <u>four</u> different hydrogen environments. (The NMR spectrum is incorrect as the triplet should be a doublet. Assigning the peaks was not part of the answer)

Question 4 (14 marks)

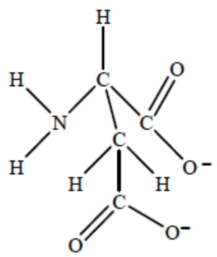
a) 1 mark for correct structure, all bonds MUST be shown to obtain the mark



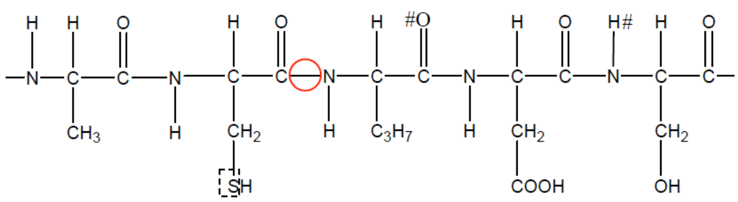
b) Amino acids contain a carboxyl –COOH functional group as well as an amino group.
DMMA molecules do not have carboxyl groups. *

c) 2-aminopropanoic acid *

d) * all bonds MUST be shown and both –COOH groups deprotonated

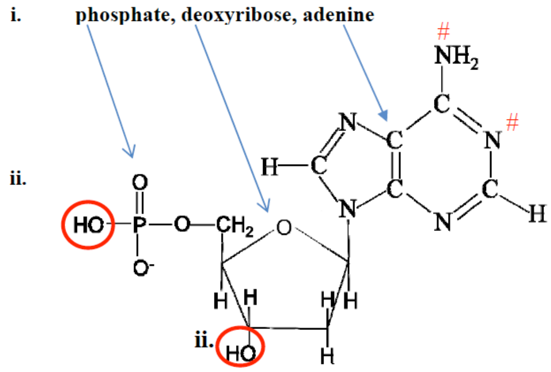


e)



i. * for any C-N bond. (the bond not the entire peptide group needed to be circled)
ii. * for an ‘O’ on one peptide group AND an ‘H’ on a <u>different</u> peptide group.
iii. *for the ‘S’ atom.

f)



Names of all species were available from the data booklet

i ** for all three correct, [* for two correct]

ii. * for both 'OH' groups circled. Also accept POOH.

iii. * for both the N and the NH_2 on the right hand side of the nitrogen base (adenine). No marks if the H on the C-H is asterisked.

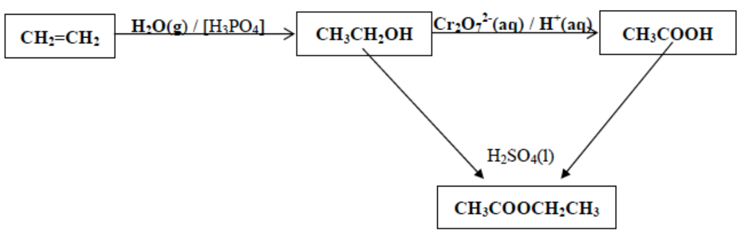
g) Adenine-Thymine (A-T) pairs have only two sites for hydrogen bonding. * The *greater* the proportion of C-G (cytosine-guanine) base pairs, the *stronger* the attraction between the strands.

Question 5 (13 marks)

a) The two peaks are in the absorption band 1670-1750 cm^{-1} (Data Book) and are caused by the **two** C=O groups * in the molecule. The peaks are centered at slightly different wavenumbers because of the different bonding environments in the caffeine molecule; one C=O is between two N atoms whilst the other C=O is between one C and one N atom. *

b) There are eight peaks and there are 8 'different' carbon atoms * in the caffeine molecule. Each C atom has a different bonding environment (looking through the whole molecule) *

c)



Two marks ** for the four correct semi-structural formulae; one mark if two or three correct.

One mark * for $H_2O(g)$ / $[H_3PO_4]$ (H_2O has to be (g) because it is steam)

One mark * $Cr_2O_7^{2-}(aq)$ / $H^+(aq)$ (no mark if **not** acidic conditions)

One mark * $H_2SO_4(l)$ (no mark if no or aq state)

e) $CH_3CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ *

Correct states and equilibrium arrows necessary for the mark (no half mark!)

$H_2SO_4(l)$ as catalyst needed

f) i. Because the forward reaction is endothermic, the yield of ethyl ethanoate will be increased. *

The higher temperature will increase the rate of reaction. *

ii. Ethanol is volatile and very flammable and should not be used near a naked flame. There would be a high risk of explosion. *

(Ethanoic acid is also flammable)

Question 6 (18 marks)

a) The radioactive hydrogen will participate in the equilibrium, i.e. it will react with iodine at the same rate that HI will be broken down.*
Radioactive HI should be detected as the forward and reverse reactions will continue even though there is no evident concentration change.*

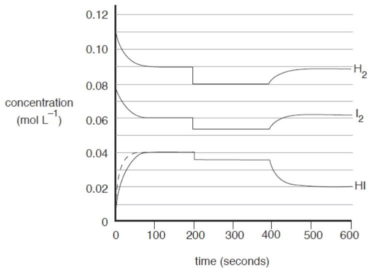
b) $K = [HI]^2 / [H_2]\mathbf{x}[I_2]$ * = $(0.04)^2 / (0.09)\mathbf{x}(0.06)$ * = 0.3* (1SF)

c) As the gaseous concentrations decreased, the volume of the equilibrium container was increased. *
The concentration of H_2 decreased from 0.090 M to 0.080 M, so the volume was increased by a factor of 9/8. * (magnitude has to be given to obtain full mark)

d) **i.** lower *

ii. The concentrations of the reactants increase and the concentration of the product decreases. *
In the concentration fraction, the numerator is smaller and the denominator is larger, resulting in a smaller value of **K**.

e) Drawing on graph should show equilibrium concentration of 0.040 M being reached earlier.



f) i. $\Delta H = \Delta H_1 + \Delta H_2 = -180 + 66 = -114\ kJ\ mol^{-1}$

ii. $K = [NO_2]^2 / [NO]^2 \times [O_2]$ *

iii. The equilibrium constant for the reaction can be obtained from the equilibrium constants for other two reactions.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_1 = 6.7\times10^{-10}$$

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad K_2 = 3.1\times10^{-9}\ M^{-1}$$

$$\frac{[NO]^2}{[N_2][O_2]} = 6.7\times10^{-10}$$

$$\frac{[NO_2]^2}{[N_2][O_2]^2} = 3.1\times10^{-9}$$

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} / \frac{[NO]^2}{[N_2][O_2]} \textbf{ (1 mark)}$$

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]} = 3.1\times10^{-9} / 6.7\times10^{-10} = \mathbf{4.6\ M^{-1}} \textbf{ (1 mark)}$$

Alternative solution:

The chemical equation for the required reaction is:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Since the starting material in this reaction is nitrogen(II) oxide then the chemical equation and equilibrium constant for the decomposition of nitrogen(II) oxide into nitrogen and oxygen will be

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad K_1^* = 1/6.7\times10^{-10}$$

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad K_2 = 3.1\times10^{-9}\ M^{-1}$$

The equilibrium constant for this reaction will be the product of the two equilibrium constants, K_1^* and K_2 above.

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]} = 3.1\times10^{-9} \times (1/6.7\times10^{-10}) = 4.6\ M^{-1}$$

iv. The rates of the two reactions would be expected to be slow because both reactions involve *breaking the nitrogen-nitrogen triple bond* ½* which would *require a large amount of energy* ½* Therefore the activation energies for these reactions would be large.

v. 1 mark for correct energy level of reactants and product (reactants higher energy value than products b/c exothermic reaction)
½* correct labelling of E_A (forward and backward reaction)
½* correct labelling of ΔH

Consequential marks possible if ΔH in f) was determined as positive.

Question 7 (6 marks)

a) The volume of hydrogen gas is doubled so the mass of magnesium must have been doubled. *
(An increase in acid concentration, or a temperature rise are not correct responses.)

b) Possible changes include:
- decreasing the magnesium surface area by adding it as a ball *
- reducing the volume of the acid *
- reducing the concentration of acid *
- adding less magnesium*

c) - change in mass of the reactor over time *
- the change in pH of the solution over time*

Question 8 (11 marks)

a) biodiesel structural formula: (not drawn here due to space…)
$C_{17}H_{35}COOCH_3$ * (all bonds need to be shown to obtain full marks, lone pairs not necessary)

b) ester linkage *

c) $2C_{17}H_{35}COOCH_3(s) + 55O_2(g) \rightarrow 38CO_2(g) + 38H_2O(g)$ * (all needs to be correct to obtain the 1 mark)

d) $E = c_f \times \Delta T = 1175 \times 15.83 = 18.60$ kJ *
$M_{biodiesel} = 298.5$ g/mol
$n_{biodiesel} = 0.50 / 298 = 0.00168$ mol *
18.6 kJ per 0.00168 mol therefore
ΔH_c = **-1.1×10^4 kJ/mol** ** (-1 mark if not a negative value)

e) ΔH_c (butane) from the data booklet = –2874kJ/mol
n(butane) = 10g / 58gmol^{-1} = **0.17 mol** *
Energy released: E = **4.9×10^2 kJ*** (energy value has to be positive!)

e) Energy released by10g butane = **4.9×10^2 kJ**
Energy released by 10g biodiesel = **3.7×10^2 kJ**
Therefore the energy released by the biodiesel is slightly **less** than butane*

f) biodiesel is a solid so easier to transport *

Question 9 (9 marks)

Note: The electrodes in the diagram were NOT labelled with A and B. I went through all the rooms and told students to label them so answer **a)** and **b)** could be the other way around but have to be correct and written as below:

a) $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ *

b) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ *

c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ *

d) Anode. Oxidation (loss of electrons) occurs at the anode*

e) Electrical energy *

f) No harmful emissions *

g) Does not have a continuous supply of reactants ½* and Al is not considered a fuel ½*

h) Advantage: one of the following: *
- higher efficiency, continual supply of energy, long lasting, not polluting (rechargeable is incorrect)

Disadvantage: one of the following *

- very expensive, needs continual fuel addition, high temperature etc