2006 National Qualifying Exam – Chemistry
Solutions

Section A (Multiple Choice)

Question #	Answer	Question #	Answer	Question #	Answer
Q1	B	Q6	B	Q11	C
Q2	D	Q7	C	Q12	C
Q3	D	Q8	B	Q13	A
Q4	C	Q9	D	Q14	A
Q5	E	Q10	E	Q15	E

Question 16

(a) **[2 marks]**

Mg > Zn > Pb > Cu

(b) **[1 mark]**

Mg

(c) **[3 marks]**

Reduction half equation: $Pb^{2+} + 2e^- \rightarrow Pb$

Oxidation half equation: $Zn \rightarrow Zn^{2+} + 2e^-$

Redox equation: $Zn + Pb^{2+} \rightarrow Zn^{2+} + Pb$

(d) **[1 mark]**

Zn

(e) **[4 marks]**

Fe in $K_3[Fe(CN)_6]$ (hint: CN has a charge of –1)	+3
Fe in $K_2M_3[Fe(CN)_6]_2$	+2
S in $K_2S_2O_3$	+2
S in $S_4O_6^{2-}$	+2½

(f) **[6 marks]**

Reduction half equation	$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$ x 2
Oxidation half equation	$3I^- \rightarrow I_3^- + 2e^-$
Full equation	$2Fe(CN)_6^{3-} + 3I^- \rightarrow 2Fe(CN)_6^{4-} + I_3^-$

(g) **[2 marks]**

$2Fe(CN)_6^{4-} + 2K^+ + 3X^{2+} \rightarrow K_2X_3[Fe(CN)_6]_2$

(h) **[1 mark]**

1 x 2/3 x 1/2 = 2/6 = 1/3

(i) **[4 marks]**

Reduction half equation

$I_3^- + 2e^- \rightarrow 3I^-$

Oxidation half equation

$2S_2O_4^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

Full equation

$I_3^- + 2S_2O_4^{2-} \rightarrow 3I^- + S_4O_6^{2-}$

(j) **[1 mark]**

1/3 (from part iv) x 2/1 = 2/3

(k) **[2 marks]**

$n(S_2O_4^{2-}) = c(S_2O_4^{2-}) \times v(S_2O_4^{2-})$
$= .0231 \times .100$
$= 2.31 \times 10^{-3}$ mol
$n(X^{2+}) = 3/2 \times n(S_2O_4^{2-})$
$= 3/2 \times 2.31 \times 10^{-3}$ mol
$= 3.465 \times 10^{-3}$ mol
$[X(NO_3)_2] = [X^{2+}] = n(X^{2+})/v(X^{2+})$
$= 3.465 \times 10^{-3} / 0.0250$
$= 1.386 \times 10^{-2}$
$= 1.39 \times 10^{-2}$ M

(l) **[3 marks]**

$[X(NO_3)_2]_{true} = [X(NO_3)_2]_{false} \times 100/99.3 \times 100/99.4$
$= 1.386 \times 10^{-2} \times 100/99.3 \times 100/99.4$
$= 1.40 \times 10^{-2}$ M

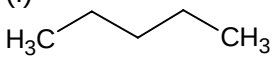
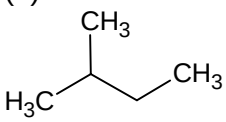
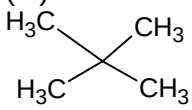
Question 17 [**2 marks**]

$^{12}_{6}C$ $^{14}_{6}C$ $\boxed{^{14}_{7}N}$ $\boxed{^{15}_{8}O}$ $^{16}_{8}O$ $\boxed{^{19}_{9}F}$ $\boxed{^{31}_{15}P}$ $\boxed{^{195}_{78}Pt}$

(a) [**3 marks**]

(a) 4	4	4
(b) 4	4	5

(b) [**3 marks**]

(I) 	(II) 	(III) 

(c) [**3 marks**]

(I) ^{1}H NMR: 3 ^{13}C NMR: 3	(II) ^{1}H NMR: 4 ^{13}C NMR: 4	(III) ^{1}H NMR: 1 ^{13}C NMR: 2

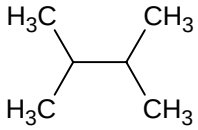
(d) [**2 marks**]

$$\text{C:H} = \frac{83.6}{12.01} : \frac{16.4}{1.008}$$
$$= 6.96 : 16.27$$
$$= 1 : 2.33$$
$$= 3 : 7$$
$$\rightarrow C_3H_7$$

(e) [**1 marks**]

Mass of C_3H_7 = 43.1 g
→2 units required for molecule
→ C_6H_{14}

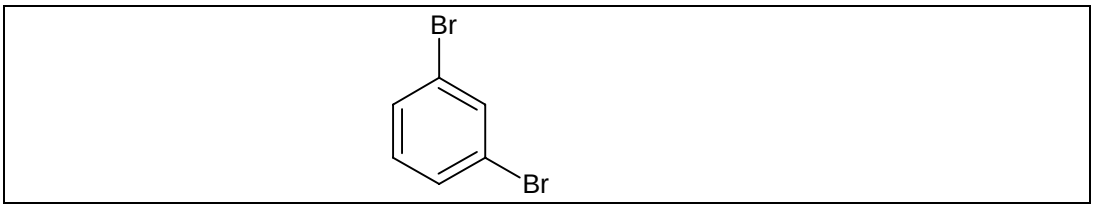
(f) [**2 marks**]



(g) [**2 marks**]

meta ^{1}H NMR: 5 ^{13}C NMR: 7	*para* ^{1}H NMR: 3 ^{13}C NMR: 5

(h) [**2 marks**]



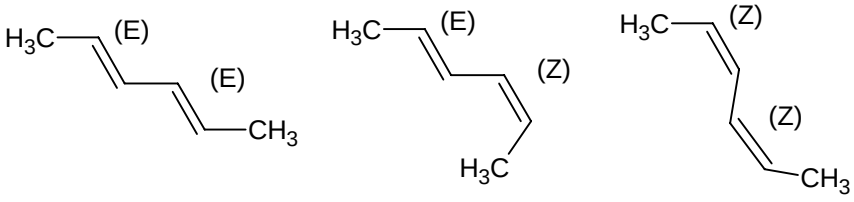
(i) [**1 marks**]

4

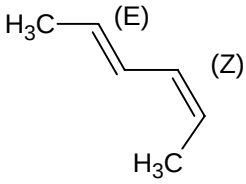
(j) **[1.5 marks]**

E	Z	Z

(k) **[4.5 marks]**

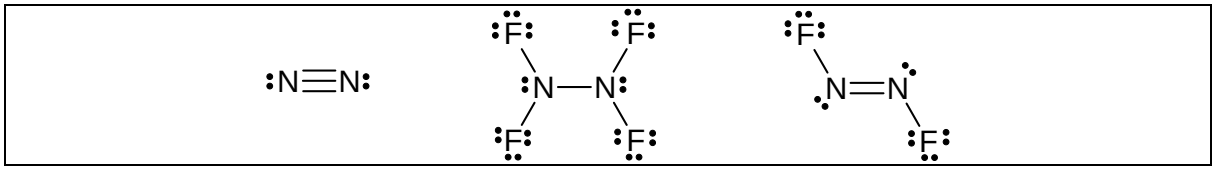


(l) **[3 marks]**



Question 18

(a) **[3 marks]**



(b) **/1 mark**

$N_2 < N_2F_2 < N_2F_4$

(c) **/1 mark**

$N_2F_4 < N_2F_2 < N_2$

(d) **[2 marks]**

$151\ kJ\ mol^{-1} / 6.02 \times 10^{23}\ mol^{-1} = 2.50_7 \times 10^{-19}\ J$

$2.50_7 \times 10^{-19}\ J / 1.602 \times 10^{-19}\ J\ eV^{-1} =$ **1.56 eV**

(e) **[1 mark]**

It will oscillate between **99** and **433 pm**.

(f) **[2 marks]**

A bond length of 0 is impossible because of the Coulombic repulsion between the nuclei, so the bond energy should go to infinity as the bond length approaches zero.

(g) **[2 marks]**

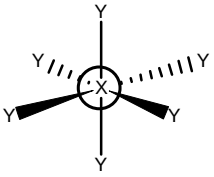
A bond length of infinity corresponds to two non-bonded atoms, so the bond energy should approach a constant as the bond length goes to zero, reflecting the fact that there is less and less interaction between the atoms at this distance.

(h) **[3 marks]**

Oops – the intention here was to have 1 mark for each of the features in (c), (e) and (f). Unfortunately the scale is completely wrong for drawing a bond with a dissociation energy of 1.57 eV! Sorry. Under the circumstances 1.5 marks were given to each for the features in (f) and (g), and ignore the dissociation energy entirely.

(i) **[4 marks]**

No COS 

No COS 

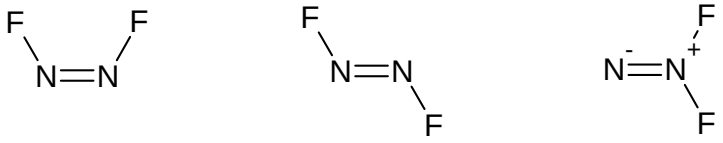
(j) **[2 marks]**

TiF_2 is bent. Since it absorbs the same frequencies in its IR and Raman spectra, it cannot have a COS.

(k) **[2 marks]**

XeF_4 doesn't have any peaks common to both spectra. While this could just be a coincidence, it's more likely (and in fact true) that these are prohibited by the rule of mutual exclusion, which means that it must have a COS and therefore be square planar.

(l) **[3 marks]**



(m) **[2 marks]**

Again, there are no peaks common to both spectra. While this could just be a coincidence, with so many peaks it's most likely that these are prohibited by the rule of mutual exclusion, which means that it must have a COS. The only isomer of the ones above which has a COS is the *trans* isomer.

(n) **[2 marks]**

By the rule of mutual exclusion, N_2O *can't* have a COS. Since we know it's linear, the atoms must be bonded in the order NNO.

Question 19

(a) **[2 marks]**

A large value of K_c indicates that the solute favours the stationary phase and moves slowly through the column.

(b) **[2 marks]**

Mobile phase: $[A] = 10/2 \times 10^6\ nm^3 = 5 \times 10^{-6}$ molecules/nm^3
$[B] = 2/2 \times 10^6\ nm^3 = 1 \times 10^{-6}$ molecules/nm^3 } 0.5 marks

Stationary phase: $[A] = 10/5 \times 10^4\ nm^3 = 2 \times 10^{-4}$ molecules/nm^3
$[B] = 7/5 \times 10^4\ nm^3 = 1.4 \times 10^{-4}$ molecules/nm^3 } 0.5 marks

K_c (A) = $[A]_S/[A]_M = 2 \times 10^{-4}/5 \times 10^{-6}$ = **40** 0.5 marks

K_c (B) = $[B]_S/[B]_M = 1.4 \times 10^{-4}/1 \times 10^{-6}$ = **140** 0.5 marks

(c) [**2 marks]**

The solute emerges from the column at a time very close to the dead time (t_M).

(d) **[2 marks]**

$$R_s = \frac{2(17.63-16.40)}{(1.11+1.21)} = \mathbf{1.06}$$

(e) **[4 marks]**

$$N_A = 16\left(\frac{16.40}{1.11}\right)^2 = \mathbf{3493};\quad N_B = 16\left(\frac{17.63}{1.21}\right)^2 = \mathbf{3397}$$

$$N_A = \frac{3493+3397}{2} = \mathbf{3445}$$

(f) **[2 marks]**

$H = L/N = 30.0\ cm/3445$ **$= 8.71 \times 10^{-3}$ cm**

(g) **[6 marks]**

$$\frac{(R_s)_1}{(R_s)_2} = \frac{\sqrt{N_1}}{\sqrt{N_2}}$$

$$\frac{1.06}{1.5} = \frac{\sqrt{3445}}{\sqrt{N_2}}$$

$$N_2 = 3445\left(\frac{1.5}{1.06}\right)^2 = \mathbf{6.9 \times 10^3}$$

$$L = N \times H = 6.9 \times 10^3 \times 8.7 \times 10^{-3} = \mathbf{60cm}$$

(h) **[2 marks]**

So that the ODS group is not "stripped" from the silica support as a result of the high pressures developed during HPLC.

(i) **[2 marks]**

Eluted first		Eluted last
Butan-1-ol	diethyl ether	hexane

[1 mark for the reverse order]

(j) **[4 marks]**

Time (hour)	**Peak Area**	**Ibuprofen Concentration ($\mu g\ mL^{-1}$)**
0	0	**0**
0.5	91.3	**14.2**
1.0	80.2	**12.2**
1.5	52.1	**7.6**
2.0	38.5	**5.6**
3.0	24.2	**3.2**
4.0	21.2	**2.8**
6.0	18.5	**2.4**
8.0	15.2	**2.0**

(k) **[2 marks]**

Third half hour or between 1 and 1.5 hours.