2011 CHEMISTRY NATIONAL QUALIFYING EXAMINATION
SOLUTIONS

SECTION A: MULTIPLE CHOICE
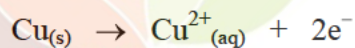
Question	Answer	Question	Answer
1	A	9	A
2	E	10	C
3	D	11	B
4	B	12	B
5	C	13	A
6	D	14	E
7	D	15	D
8	B		

SECTION B: SHORT ANSWER QUESTIONS

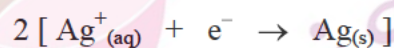### Question 16

(a)

Oxidation

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$$

Reduction

$$2[Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}]$$

Redox

$$Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

(b)

$$Ag_{(s)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} + e^-$$

(c)

$$Mo^{6+}_{(aq)} + e^- \rightarrow Mo^{5+}_{(aq)}$$

$$Ag_{(s)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} + e^-$$

$$Mo^{6+}_{(aq)} + Ag_{(s)} + Cl^-_{(aq)} \rightarrow Mo^{5+}_{(aq)} + AgCl_{(s)}$$
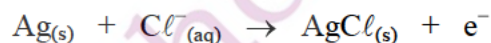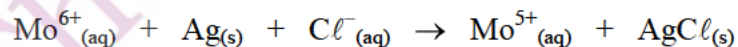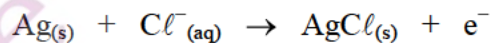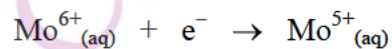
(d)

The hydrochloric acid solution provides the chloride ions (Cl^-) necessary to oxidise silver metal to silver chloride.
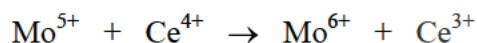
(e)

The molybdate solution is heated in order to increase the rate of reaction (to help ensure complete reaction as the solution passes through the silver reductor).

(f)

The dark coating is the result of the photodecomposition of silver chloride.

(g)

$$Mo^{5+} + Ce^{4+} \rightarrow Mo^{6+} + Ce^{3+}$$

$n(Ce^{4+}) = 0.116 \times 0.02441$

$n(Ce^{4+}) = 2.832 \times 10^{-3} mol$

$n(Mo^{5+})_{reacted} = 2.832 \times 10^{-3} \times \dfrac{1}{1}$

$n(Mo^{5+})_{reacted} = 2.832 \times 10^{-3} mol$

$n(Mo)_{total} = 2.832 \times 10^{-3} \times \dfrac{250}{50}$

$n(Mo)_{total} = 1.416 \times 10^{-2} mol$

$n(Mo)_{total} = 1.42 \times 10^{-2} mol$

h)

$FW = (14.01 + 4 \times 1.008) \times 6 + 95.94\,x + 16.00\,y + 4 \times (2 \times 1.008 + 16.00)$

$FW = 180.316 + 95.94\,x + 16.00\,y$

(i)

For the sample,

$n(Mo) = x \left[\dfrac{m(Mo)}{FW(Mo)} \right]$,

Which, using the equation from (h) and the mass given in the question, becomes

$n(Mo) = x \left[\dfrac{2.50}{180.316 + 95.94\,x + 16.00\,y} \right]$.

From the titration data we have also already calculated the amount of molybdenum in the sample to be 1.416×10^{-2} mol. Thus the equation becomes

$1.416 \times 10^{-2} = x \left[\dfrac{2.50}{180.316 + 95.94\,x + 16.00\,y} \right]$ **Equation 1**

By summing the charges of each of the species in the formula for ammonium molybdate it is possible to form the following equation.

$1 \times 6 = 6x - 2y = 0$

Which can be simplified to

$y = 3x - 3$ **Equation 2**

Solving equations 1 and 2 simultaneously for x gives

$$x = \frac{228.316}{\dfrac{2.50}{1.416 \times 10^{-2}} - 143.94}$$

$x = 7.00$
and substituting back into equation 2 gives
$y = 24$

Hence the formula of ammonium molybdate is $(NH_4)_6Mo_7O_{24}.4H_2O$

Question 17

(a)   I = Ar; O = He and P = Ne

(b)   E = F (fluorine)
        $G = C\ell$
        J = N
        S = H
        Q = O (oxygen)
        Y = Br
        Z = I (iodine)

(c)   D = Na
        H = K
        L = Ca
        R = Li

(d)   B = Mg
        $C = A\ell$
        K = Be

(e)   A = P (phosphorus)
        F = S (sulphur)
        M = B (boron)
        N = C (carbon)
        T = Si (silicon)

(f) Nb_2O_5 and $NbC\ell_5$ and $NbOC\ell_3$
        X = Nb

Question 18

(a)
(i) and (ii)

2→3: 656 nm
2→5: 434 nm

(iii) $E = 3.03 \times 10^{-19}$ J (1.89 eV)

(iv) As n increases, the wavelength increases.
Wavelength is inversely proportional to energy, thus the energy decreases

(v) The spectrum shows n=2→3 to n=2→6 transitions. As n increases, the difference in wavelength between two $\Delta n = 1$ transitions will decrease. This explains the clumping on the left hand side of the spectrum.

(b)

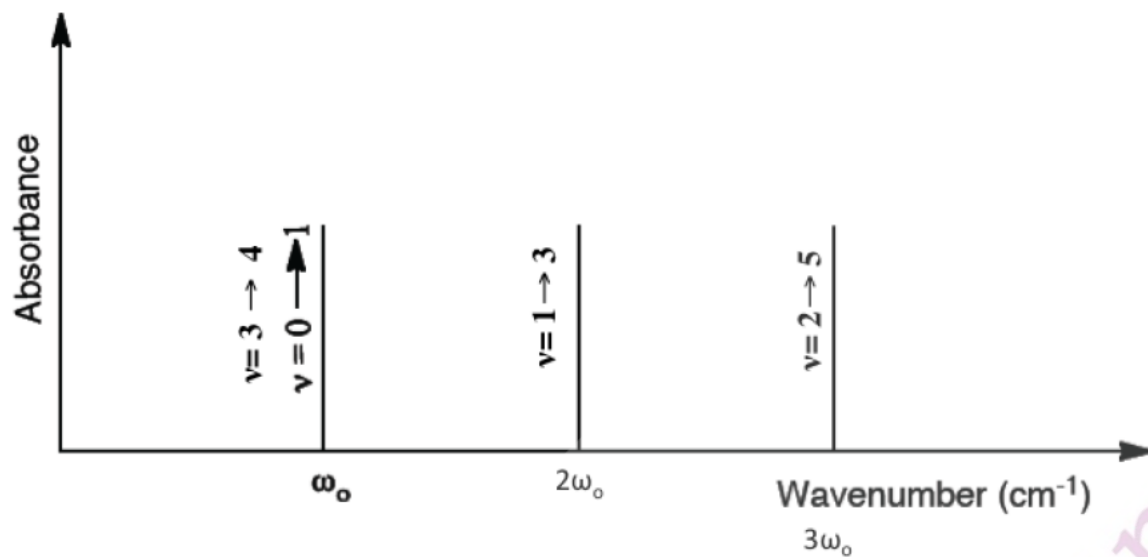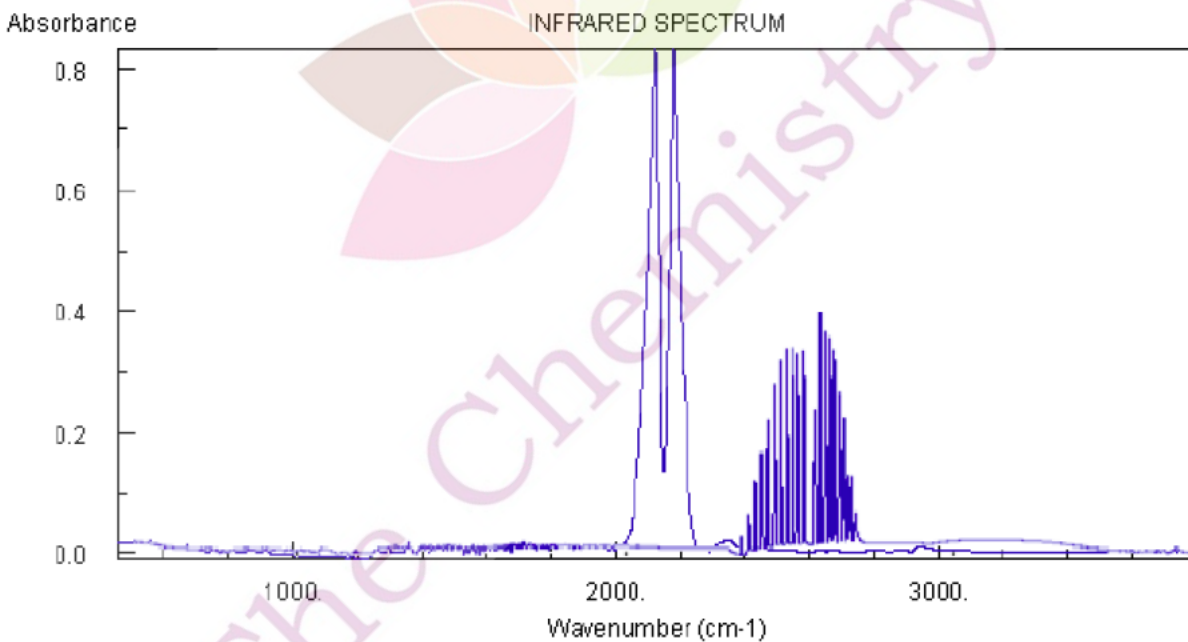| Molecule	Ne	O_2	C_2H_4
Lewis Structure	$:\overset{..}{\underset{..}{Ne}}:$	$:\overset{}{O}=\overset{..}{\underset{..}{O}}:$	
Total DoF	3	6	18
Vibrational	0	3	3
Translational	3	3	3
Rotational	0	1	12

(c)
(i) $\mu = 1.62 \times 10^{-27}$ kg

(ii) $E = 5.93 \times 10^{-19}$ J (0.37 eV)

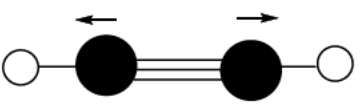(iii) $\Delta E = \hbar\omega$ for $\Delta v = 1$. Note this is independent of v!
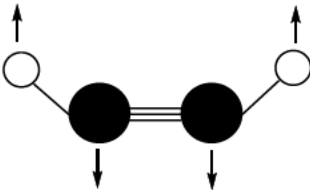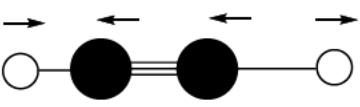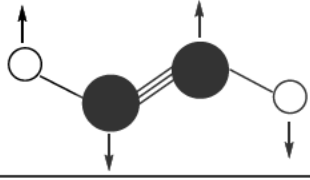
(iv)

(d) N_2 has no dipole moment and therefore is not in the spectrum.
        HBr has a reduced mass of 0.987 amu. Therefore, $k/\mu = 415$.
        CO has a reduced mass of 6.857 amu. Therefore, $k/\mu = 271$.
        Hence, HBr will appear at the higher wavenumber.

(e)

Mode			
Type	*Stretch #1*	*Bend #1*	*Stretch #2*
IR Active	☐Yes X No	☐Yes X No	☐Yes X No

Mode		
Type	*Stretch #3*	*Bend #2*
IR Active	XYes ☐ No	XYes ☐No

(f)
(i)
HCN (linear)

(ii)
4

(iii)
The four possible vibrational modes are:
-   two stretches as there are two connections between atoms,
-   two bends which are equivalent but operate in different directions. If we align the molecule along a y-axis, the molecule can bend along the z and x-axes.

If we consider $\sqrt{k/\mu}$ ratios for the stretches, the C-H stretch is about 1.5 times larger than the C-N stretch. Hence, this fits with the excitations at 2000 **(B)** and 3500 cm^{-1} **(C)**. By deduction, **A** must be a bend.

A: bend
B: C–N stretch
C: H–C stretch

(iv) Note there is a peak at around 1400 cm^{-1} which is approximately double the wavenumber at **A**. This is a $\Delta v=2$ transition for the bend