## 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

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

Reduction

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

Redox

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

(b)

$$
\mathrm{Ag}_{(\mathrm{s})}+\mathrm{C}^{-}{ }_{(\mathrm{aq})} \rightarrow \mathrm{AgCl}_{(\mathrm{s})}+\mathrm{e}^{-}
$$

(c)

$$
\begin{aligned}
& \mathrm{Mo}^{6+}{ }_{(\mathrm{aq})}+\mathrm{e}^{-} \rightarrow \mathrm{Mo}^{5+}{ }_{(\mathrm{aq})} \\
& \mathrm{Ag}_{(\mathrm{s})}+\mathrm{C}^{-}{ }_{(\mathrm{aq})} \rightarrow \mathrm{AgCl}_{(\mathrm{s})}+\mathrm{e}^{-} \\
& \mathrm{Mo}^{-----------------------------------------------------------}{ }_{(\mathrm{aq})}+\mathrm{Ag}_{(\mathrm{s})}+\mathrm{C}^{-}{ }_{(\mathrm{aq})} \rightarrow \mathrm{Mo}^{5+}{ }_{(\mathrm{aq})}+\mathrm{AgC} \ell_{(\mathrm{s})}
\end{aligned}
$$

(d)

The hydrochloric acid solution provides the chloride ions ( $\mathrm{C} \ell^{-}$) 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)

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

$$
\begin{aligned}
& \mathrm{n}\left(\mathrm{Ce}^{4+}\right)=\begin{array}{lll}
0.116 & 0.02441 \\
\mathrm{n}\left(\mathrm{Ce}^{4+}\right)=2.832 & 10^{-3} \mathrm{~mol} \\
\mathrm{n}\left(\mathrm{Mo}^{5+}\right)_{\text {reacted }}=2.832 & 10^{-3} & \frac{1}{1} \\
\mathrm{n}\left(\mathrm{Mo}^{5+}\right)_{\text {reacted }}=2.832 & 10^{-3} \mathrm{~mol} \\
\mathrm{n}(\mathrm{Mo})_{\text {total }}=2.832 & 10^{-3} & \frac{250}{50} \\
\mathrm{n}(\mathrm{Mo})_{\text {total }}=1.416 & 10^{-2} \mathrm{~mol} \\
\mathrm{n}(\mathrm{Mo})_{\text {total }}=1.42 & 10^{-2} \mathrm{~mol}
\end{array}
\end{aligned}
$$

h)

$$
\begin{aligned}
& \mathrm{FW}=\left(\begin{array}{ll}
14.01+4 & 1.008
\end{array}\right) \quad 6+95.94 \mathrm{x}+16.00 \mathrm{y}+4 \quad\left(\begin{array}{ll}
2 & 1.008+16.00
\end{array}\right) \\
& \mathrm{FW}=180.316+95.94 \mathrm{x}+16.00 \mathrm{y}
\end{aligned}
$$

(i)

For the sample,
$\mathrm{n}(\mathrm{Mo})=\mathrm{x} \frac{\mathrm{m}(\mathrm{Mo})}{\mathrm{FW}(\mathrm{Mo})} \dot{\text {, }}$
Which, using the equation from (h) and the mass given in the question, becomes
$n(M o)=x \frac{2.50}{180.316+95.94 x+16.00 y} \div$.
From the titration data we have also already calculated the amount of molybdenum in the sample to be $1.416 \times 10^{-2} \mathrm{~mol}$. Thus the equation becomes
$1.416 \quad 10^{2}=x \frac{2.50}{180.316+95.94 x+16.00 y} \div$ 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.
$1 \quad 6+6 x \quad 2 y=0$
Which can be simplified to
$y=3 x+3 \quad$ Equation 2

Solving equations 1 and 2 simultaneously for x gives
$x=\frac{228.316}{\frac{2.50}{1.41610^{2}} 143.94}$
$x=7.00$
and substituting back into equation 2 gives
$y=24$
Hence the formula of ammonium molybdate is $\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \cdot 4 \mathrm{H}_{2} \mathrm{O}$

## Question 17

(a) $\mathrm{I}=\mathrm{Ar} ; \mathrm{O}=\mathrm{He}$ and $\mathrm{P}=\mathrm{Ne}$
(b) $\mathrm{E}=\mathrm{F}$ (fluorine)
$\mathrm{G}=\mathrm{C} \ell$
$\mathrm{J}=\mathrm{N}$
$\mathrm{S}=\mathrm{H}$
$\mathrm{Q}=\mathrm{O}$ (oxygen)
$\mathrm{Y}=\mathrm{Br}$
$\mathrm{Z}=\mathrm{I}$ (iodine)
(c) $\mathrm{D}=\mathrm{Na}$
$\mathrm{H}=\mathrm{K}$
$\mathrm{L}=\mathrm{Ca}$
$\mathrm{R}=\mathrm{Li}$
(d) $\mathrm{B}=\mathrm{Mg}$
$\mathrm{C}=\mathrm{A} \ell$
$\mathrm{K}=\mathrm{Be}$
(e) $\mathrm{A}=\mathrm{P}$ (phosphorus)
$\mathrm{F}=\mathrm{S}$ (sulphur)
$\mathrm{M}=\mathrm{B}$ (boron)
$\mathrm{N}=\mathrm{C}$ (carbon)
$\mathrm{T}=\mathrm{Si}$ (silicon)
(f) $\mathrm{Nb}_{2} \mathrm{O}_{5}$ and $\mathrm{NbC} \ell_{5}$ and $\mathrm{NbOC}_{3}$
$\mathrm{X}=\mathrm{Nb}$

## Question 18

(a)
(i) and (ii)
$2 \rightarrow 3$ : 656 nm
$2 \rightarrow 5$ : 434 nm
(iii) $\mathrm{E}=3.03 \times 10^{-19} \mathrm{~J}(1.89 \mathrm{eV})$
(iv) As n increases, the wavelength increases.

Wavelength is inversely proportional to energy, thus the energy decreases
(v) The spectrum shows $\mathrm{n}=2 \rightarrow 3$ to $\mathrm{n}=2 \rightarrow 6$ transitions. As n increases, the difference in wavelength between two $\Delta \mathrm{n}=1$ transitions will decrease. This explains the clumping on the left hand side of the spectrum.
(b)

| Molecule | Ne | $\mathrm{O}_{2}$ | $\mathrm{C}_{2} \mathrm{H}_{4}$ |
| :---: | :---: | :---: | :---: |
| Lewis Structure | : Ne: | $: 0=0:$ |  |
| Total DoF | 3 | 6 | 18 |
| Vibrational | 0 | 3 | 3 |
| Translational | 3 | 3 | 3 |
| Rotational | 0 | 1 | 12 |

(c)
(i) $\quad \mu=1.62 \times 10^{-27} \mathrm{~kg}$
(ii) $\mathrm{E}=5.93 \times 10^{-19} \mathrm{~J}(0.37 \mathrm{eV})$
(iii) $\Delta \mathrm{E}=\mathrm{h} \omega$ for $\Delta v=1$. Note this is independent of $v$ !
(iv)

(d) $\quad \mathrm{N}_{2}$ has no dipole moment and therefore is not in the spectrum.

HBr has a reduced mass of 0.987 amu . Therefore, $\mathrm{k} / \mu=415$.
CO has a reduced mass of 6.857 amu . Therefore, $\mathrm{k} / \mu=271$.
Hence, HBr will appear at the higher wavenumber.

(e)

| Mode |  |  |  |
| :---: | :---: | :---: | :---: |
| Type | Stretch \#1 | Bend \#1 | Stretch \#2 |
| IR Active | $\square \mathrm{Yes} \mathrm{X} \mathrm{No}$ | $\square \mathrm{Yes} \mathrm{X} \mathrm{No}$ | $\square \mathrm{Yes} \mathrm{X} \mathrm{No}$ |
| Mode |  |  |  |
| Type | Stretch \#3 | Bend \#2 |  |
| IR Active | XYes $\square$ No | XYes $\square$ 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 $\sqrt{ } / \mu$ ratios for the stretches, the C-H stretch is about 1.5 times larger than the $\mathrm{C}-\mathrm{N}$ stretch. Hence, this fits with the excitations at 2000 (B) and $3500 \mathrm{~cm}^{-1}$ (C). By deduction, A must be a bend.

A: bend
B: $\mathrm{C}-\mathrm{N}$ stretch
C: $\mathrm{H}-\mathrm{C}$ stretch
(iv) Note there is a peak at around $1400 \mathrm{~cm}^{-1}$ which is approximately double the wavenumber at A. This is a $\Delta v=2$ transition for the bend

