## FUNDAMENTALS OF CHEMISTRY 1B (CHEM1002)

November 2001 - Part A
Q1. $\quad \mathrm{As}_{2} \mathrm{O}_{3}$ potassium permanganate
$\mathrm{KCH}_{3} \mathrm{CO}_{2}$ hexaaquairon(II) ion $\mathrm{Na}_{2}\left[\mathrm{CuCl}_{4}\right]$ sodium dicyanoargentate(I) $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3} \mathrm{Cl}_{3}\right]$ ammonium chloride $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$ triaquachlorocopper(II) ion

Q2. (a) (i) selenium (Se)
(ii) chlorine (Cl)
(b) (i) $1 s^{2} 2 s^{2} 2 p^{6} \quad$ (note that it's an ion)
(ii) $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6} 4 s^{1}$
(c) Paramagnetism arises from unpaired electrons.

$$
3 d \quad \begin{array}{l|l|l|l|l|l|}
\hline & \uparrow \downarrow & \uparrow \downarrow & \uparrow \downarrow & \uparrow & \uparrow \\
\hline
\end{array}
$$

$\mathrm{Ni}^{2+}$ has two unpaired electrons in the 3d orbitals
(d) $\quad \mathrm{Cl}(\mathrm{g})+\mathrm{e}^{-} \rightarrow \mathrm{Cl}(\mathrm{g}) \quad$ (NB must be gas phase)

Q3. Across a field, as more electrons occupy the same principal energy level, they are accompanied by additional protons in the nuclei. All outer electrons experience greater attraction to the nucleus (effective nuclear charge is increasing), and the radius decreases. After the noble gas in each row, the next atom (Group I) must use the next higher energy level for its last electron which is screened from the nucleus, so the radius increases sharply at that point. Repetition of this process means that the atomic radius increases down any group.
Q4.

|  | tetrahedral | trigonal pyramidal |
| :---: | :---: | :---: |
|  | octahedral | octahedral |
| $: \ddot{\mathrm{C}}$ - $\mathrm{Be}^{-\stackrel{\mathrm{C}}{\mathrm{C}} \text { : }}$ | linear | linear |

Q5.
unhybridised atomic orbitals
hybridised atomic orbitals


The $2 s, 2 p_{\mathrm{x}}, 2 p_{\mathrm{y}}$ and $2 p_{\mathrm{z}}$ orbitals of the fluorine atom undergo a mixing process called hybridisation to produce four equivalent $s p^{3}$ hybrid orbitals. Three of these orbitals already contain 2 electrons (the non-bonding pairs on the fluorine). The remaining $s p^{3}$ orbital that contains 1 electron can overlap with the $1 s$ orbital of a H atom to form a $\sigma$-bond.


Q6. $2 \mathrm{NH}_{3}+\mathrm{Ag}^{+} \rightleftharpoons\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$
The equilibrium for this reaction lies far to the right, removing most of the $\mathrm{Ag}^{+}$from the solution and converting it to the complex ion, diamminesilver(I) ion.

Q7. For elements of Period 2, the only orbitals that are energetically available are the $2 s$ and three $2 p$ orbitals, which can accommodate only 8 electrons ( 2 in each orbital). For elements in Period 3 and above, $d$ orbitals are energetically available to accommodate more electrons. This allows the valence level to expand beyond the limit of 8 electrons.
$\mathrm{SF}_{6}$ and $\mathrm{PF}_{5}$ contain 12 and 10 electrons in their valence levels, respectively.
Q8.

$\mathrm{H}^{-}$has two electrons around a single proton nucleus. There are no electrons inside the $1 s$ orbital to screen the electrons, so they both experience a high effective nuclear charge.

Q9. Buffers contain a weak acid (HA) and its conjugate base ( $\mathrm{A}^{-}$), both in significant amounts. Buffers resist change in pH by the following reactions.
$\mathrm{HA}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-} \quad$ (removes added $\mathrm{OH}^{-}$)
$\mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{HA} \quad$ (removes added $\mathrm{H}^{+}$)
The pH of the buffer is determined by the $\mathrm{p} K_{\mathrm{a}}$ of the weak acid and the ratio of [ HA ]: $\left[\mathrm{A}^{-}\right]$. The capacity of the buffer is determined by the amounts (concentrations) of HA and A- The most effective buffer has $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$as this can remove $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$equally well.

Q10. (a) (i) $\mathrm{pH}=2.43$
(ii) $\mathrm{pH}=11.12$
(b) $\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]=1.1 \mathrm{M}$

Q11. The reaction is $\quad \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaOH} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NaCH}_{3} \mathrm{CO}_{2}$ The $\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}$ion is a weak base reacting partially with water to give $\left[\mathrm{OH}^{-}\right]>10^{-7}$.

$$
\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OH}^{-}+\mathrm{CH}_{3} \mathrm{COOH}
$$

$\mathrm{Na}^{+}$ions do not change the pH .

Q12

volume $\mathrm{OH}^{-}$added
At the half equivalence point, the amount of HA consumed equals the amount of $\mathrm{A}^{-}$produced, and therefore $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$.

For a weak acid, $\mathrm{HA}, \quad K_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right] \times\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$
When $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right], K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]$and $\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}$.

Q13. From a knowledge of the titration type:
Strong acid v . strong base has equivalence point at $\mathrm{pH}=7$.
Strong acid v . weak base has equivalence point at $\mathrm{pH}<7$.
Weak acid v . strong base has equivalence point at $\mathrm{pH}>7$.
Choose an indicator that has a $\mathrm{p} K_{\mathrm{a}} \approx \mathrm{pH}$ at equivalence point.

Q14. ammonium ion < lactic acid < nitrous acid < hydrogen chloride $\mathrm{NH}_{4}{ }^{+}<\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}<\mathrm{HNO}_{2}<\quad \mathrm{HCl}$

Q15. The hydrolysis of the hydrated $\mathrm{Fe}^{3+}$ ion increases $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$to $>10^{-7} \mathrm{M}$.

$$
\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{OH}\right]^{2+}
$$

November 2001 - Part B
01-N-2


01-N-3 Many answers are possible. Biopolymers include proteins, DNA, starch, cellulose, rubber, etc. Proteins consist of polymeric chains of amino acids linked by the amide functional group (-CONH-).


Different proteins have different lengths and different R groups and different biological functions (eg as enzymes or for structure).

A: HBr in $\mathrm{CCl}_{4}$ solvent
B: hot dilute NaOH in water
C: $\mathrm{Cl}_{2}$ in $\mathrm{CCl}_{4}$ solvent
D: $\mathrm{N}\left(\mathrm{CH}_{3}\right)_{3}$
E: $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-} / \mathrm{H}^{+}$
1,2-dichlorobutane
01-N-4




(S)-
$\mathbf{a}=$ (secondary) amine
b = aromatic ring
$01-\mathrm{N}-5$

$$
\mathrm{CH}_{3} \mathrm{COOH}+\quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}
$$





