

PRACTICE PAPER

3*

Time allowed : 2 hours

Maximum marks : 35

General Instructions : Read the following instructions carefully.

- (a) There are 16 questions in this question paper. All questions are compulsory.
- (b) Section A : Q. No. 1 to 8 are objective type questions. Q. No. 1 is passage based question carrying 4 marks while Q. No. 2 to 8 carry 1 mark each.
- (c) Section B : Q. No. 9 to 12 are short answer questions and carry 2 marks each.
- (d) Section C : Q. No. 13 and 14 are short answer questions and carry 3 marks each.
- (e) Section D : Q. No. 15 and 16 are long answer questions carrying 5 marks each.
- (f) There is no overall choice. However, internal choices have been provided.
- (g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions :

The half life of a reaction is the time required for the concentration of a given reactant to reach a value that is arithmetic mean of its initial and final, or equilibrium, values. The half-life of a reaction has an exact quantitative meaning only in the following cases:

(i) For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

- (ii) For a reaction involving more than one reactant, with their concentrations in their stoichiometric ratios. In this case half-life of each reactant is same.

If the concentrations of reactants are not in their stoichiometric ratios, the half-life for the different reactants are not the same.

For second order reaction, $t_{1/2} = k^{-1}[A]_0^{-1}$

The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) In a first-order reaction $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is

(a) $\frac{\log 2}{k}$

(b) $\frac{\log 2}{k\sqrt{0.5}}$

(c) $\frac{\ln 2}{k}$

(d) $\frac{0.693}{0.5k}$

- (ii) 87.5% of the substance disintegrated in 45 minutes (first order reaction) what is its half life?

(a) 15 min

(b) 30 min

(c) 45 min

(d) 60 min

OR

Half-life period of a first order reaction is 1386 seconds. The specific rate constant of the reaction is

- (a) $0.5 \times 10^{-2} \text{ s}^{-1}$ (b) $0.5 \times 10^{-3} \text{ s}^{-1}$ (c) $5.0 \times 10^{-2} \text{ s}^{-1}$ (d) $5.0 \times 10^{-5} \text{ s}^{-1}$

(iii) For a first order reaction, the ratio between the time taken to complete 3/4th of the reaction and time taken to complete half of the reaction is

- (a) $t_{3/4} = 2t_{1/2}$ (b) $t_{3/4} = t_{1/2}$ (c) $t_{3/4} = 3t_{1/2}$ (d) $t_{3/4} = 5t_{1/2}$

(iv) The half-life of a reaction is halved as the initial concentration of the reactant is doubled. The order of reaction is

- (a) 0.5 (b) 1 (c) 2 (d) 0

Following questions (Q. No. 2 to 6) are multiple choice questions carrying 1 mark each :

2. Find the value of λ_{eq}° for potash alum.

Given : $\lambda_{m(\text{K}^+)}^{\circ} = 73.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $\lambda_{m(\text{Al}^{3+})}^{\circ} = 189 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $\lambda_{m(\text{SO}_4^{2-})}^{\circ} = 160 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

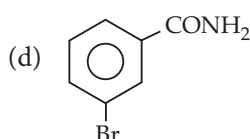
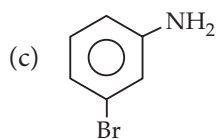
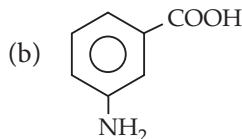
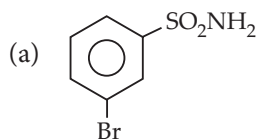
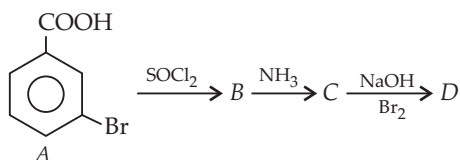
- (a) $145.6 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (b) $1165 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$
 (c) $532 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ (d) $195.5 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$

3. The correct order of reactivity of aldehydes and ketones towards hydrogen cyanide is

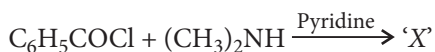
- (a) $\text{CH}_3\text{COCH}_3 > \text{CH}_3\text{CHO} > \text{HCHO}$ (b) $\text{CH}_3\text{COCH}_3 > \text{HCHO} > \text{CH}_3\text{CHO}$
 (c) $\text{CH}_3\text{CHO} > \text{CH}_3\text{COCH}_3 > \text{HCHO}$ (d) $\text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{COCH}_3$

OR

In a set of reactions *m*-bromobenzoic acid gave a product *D*. Identify the product *D*.



4. Identify 'X'.



- (a) *N,N*-Dimethylbenzamide (b) *N,N*-Dimethylbenzene
 (c) *N*-Methyl-*N*-phenylamine (d) *N,N*-Diphenylmethanamine

5. A compound of vanadium has a magnetic moment of 1.73 BM. Choose the correct electronic configuration of the vanadium ion in the compound.
- (a) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^2$ (b) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$
 (c) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$ (d) $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^0$

OR

Which of the following pairs of ions have same paramagnetic moment ?

- (a) Mn^{2+}, Cu^{2+} (b) Cu^{2+}, Ti^{3+} (c) Ti^{4+}, Cu^{2+} (d) Ti^{3+}, Ni^{2+}
6. Primary and secondary valency of platinum in the complex $[Pt(en)_2Cl_2]$ are
 (a) 4, 6 (b) 2, 6 (c) 4, 4 (d) 6, 4

In the following questions (Q. No. 7 and 8), a statement of assertion following by a statement of reason is given choose the correct answer out of the following choices :

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
 (c) Assertion is correct statement but reason is wrong statement.
 (d) Assertion is wrong statement but reason is correct statement.

7. **Assertion :** Kohlrausch law helps to find the molar conductivity of weak electrolyte at infinite dilution.
Reason : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

OR

Assertion : When a copper wire is dipped in silver nitrate solution, there is no change in the colour of the solution.

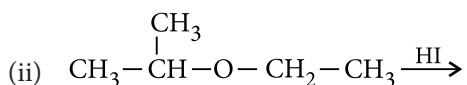
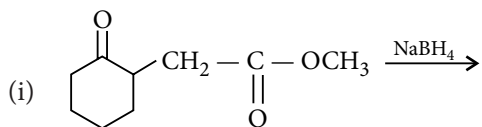
Reason : Copper can displace silver from its salt solution.

8. **Assertion :** Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
Reason : Those aldehydes which have α -H atom undergo Cannizzaro reaction.

SECTION - B

The following questions (Q. No. 9-12), are short answer type and carry 2 marks each.

9. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 is a first order reaction
 (i) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.
 (ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.
10. Write the structures of the products formed in the following reactions :



11. Explain the following :
- (a) Low spin octahedral complexes of nickel are not known.
 (b) $\Delta_t = \frac{4}{9} \Delta_o$

OR

Write the IUPAC nomenclature of the following complex along with hybridisation and structure.



12. The rate law for the reaction, $x + y \longrightarrow z$ is $r = k[x]^{3/2} [y]^{-1/2}$
Find the order and molecularity of reaction.

OR

A substance A decomposes in solution following the first order kinetics. Flask I contains 1 litre of 1 M solution of A and flask II contains 100 mL of 0.6 M solution of A. After 8 hours the concentration of A in flask I becomes 0.25 M. What will be the time for concentration of A in flask II to become 0.3 M?

SECTION - C

Q. No. 13 and 14 are short answer type II carrying 3 marks each.

13. (i) Calculate the standard electrode potential of Ni^{2+}/Ni electrode if emf of the cell
 $\text{Ni}_{(s)} | \text{Ni}^{2+} (0.01 \text{ M}) || \text{Cu}^{2+} (0.1 \text{ M}) | \text{Cu}_{(s)}$ is 0.059 V. [Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$]
(ii) Define the terms specific conductance and equivalent conductance.

OR

For M^{2+}/M and M^{3+}/M^{2+} systems, the E° values for some metals are as follows :



Use this data to comment upon :

- (i) The stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+} .
(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.
14. (a) Two moles of organic compound 'A' on treatment with a strong base give two compounds 'B' and 'C'. Compound 'B' on dehydrogenation with Cu gives 'A' while acidification of 'C' yields carboxylic acid 'D' having molecular formula of CH_2O_2 . Identify the compounds A, B, C and D.
(b) Explain Hell-Volhard-Zelinsky reaction.

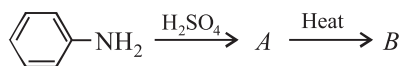
SECTION - D

Q. No. 15 and 16 are long answer type carrying 5 marks each.

15. (a) An organic compound A having molecular formula $\text{C}_2\text{H}_7\text{N}$ on treatment with HNO_2 gave an oily yellow substance. Identify 'A'. Give equation.
(b) Which amine in each of the following pairs is a stronger base? Give reason.
(i) $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$ and $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{COOCH}_3$
(ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{NHCH}_2\text{CH}_3$
(c) Account for the following :
(i) Tertiary amines do not undergo acylation reaction.
(ii) Amines are more basic than comparable alcohols.

OR

- (a) Suggest a convenient scheme for separating aniline, *N*-methylaniline, toluene and phenol present together in mixture. Distillation is not to be used.
 (b) Identify A and B.



- (c) Account for the following :
 (i) Ammonolysis of alkyl halides does not give a corresponding amine in pure state.
 (ii) If $-\text{NO}_2$ or $-\text{COOH}$ group is attached to a carbon of benzene ring, electrophilic substitution becomes difficult.

16. (a) Assign reason for the following :
 (i) The enthalpies of atomisation of transition elements are high.
 (ii) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as transition element.
 (b) What may be the possible oxidation states of the transition metals with the following d electronic configurations in the ground state of their atoms :
 $3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$. Indicate relative stability of oxidation states in each case.

OR

- (a) How would you account for the following :
 (i) The atomic radii of the metals of the third ($5d$) series of transition elements are virtually the same as those of the corresponding members of the second ($4d$) series.
 (ii) The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ couple or $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.
 (iii) The highest oxidation state of a Mn metal is exhibited in its oxide or fluoride.
 (b) Which of following cations are coloured in aqueous solutions and why?
 Sc^{3+} , V^{3+} , Ti^{4+} , Mn^{2+} (At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

ANSWERS

1. (i) (c) : For a 1st order kinetics,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{At } t_{1/2}, k = \frac{2.303}{t_{1/2}} \log \frac{a}{a-\frac{a}{2}} \Rightarrow t_{1/2} = \frac{2.303}{k} \log 2 = \frac{\ln 2}{k}$$

- (ii) (a) : $a = 100$; $a - x = 100 - 87.5 = 12.5$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{45} \log \frac{100}{12.5} = 0.046$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.046} = 15 \text{ min}$$

OR

- (b) : Given, $t_{1/2} = 1386$ s
 For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad (k = \text{rate constant})$$

$$\Rightarrow 1386 = \frac{0.693}{k} \Rightarrow k = 5 \times 10^{-4} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

$$\text{(iii) (a) : } t_{1/2} = \frac{0.693}{k}$$

$$t_{3/4} = \frac{2.303}{k} \log \left(\frac{a}{a-\frac{3a}{4}} \right) = \frac{2.303}{k} \log 4$$

$$= \frac{2.303}{k} \times 2 \times 0.310 = \frac{0.693 \times 2}{k}$$

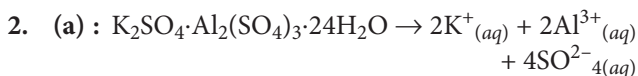
$$\frac{t_{3/4}}{t_{1/2}} = \frac{0.693 \times 2}{k} \times \frac{k}{0.693} \Rightarrow t_{3/4} = 2t_{1/2}$$

- (iv) (c) : For n^{th} order reaction,

$$t_{1/2} \propto \frac{1}{a^{n-1}} ; \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[a_2]^{n-1}}{[a_1]^{n-1}} = \left[\frac{[a_2]}{[a_1]} \right]^{n-1}$$

$$\frac{t_{1/2}}{1/2t_{1/2}} = \left(\frac{2a}{a}\right)^{n-1} \Rightarrow 2 = (2)^{n-1}$$

$$\Rightarrow (n-1) = 1 \Rightarrow n = 2$$



$$\Lambda_m^\circ(\text{Potash alum}) = 2\lambda_m^\circ(\text{K}^+) + 2\lambda_m^\circ(\text{Al}^{3+}) + 4\lambda_m^\circ(\text{SO}_4^{2-})$$

$$= 2 \times 73.5 + 2 \times 189 + 4 \times 160 = 1165 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Valency factor for potash alum = 8 (total positive charge)

$$\Lambda_{eq}^\circ(\text{Potash alum}) = \frac{\Lambda_m^\circ(\text{Potash alum})}{8} = \frac{1165}{8}$$

$$= 145.6 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

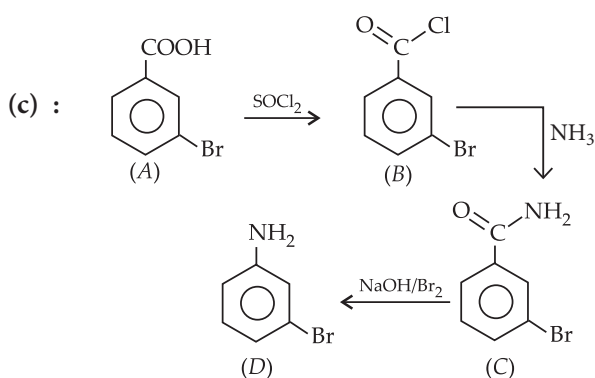
3. (d) : Alkyl group attached to carbonyl carbon increases the electron density on the carbonyl carbon and lowers its reactivity towards nucleophilic addition reactions.

Also, as the number and size of alkyl group increases, the attack of nucleophile on the carbonyl group becomes more and more difficult due to steric hindrance.

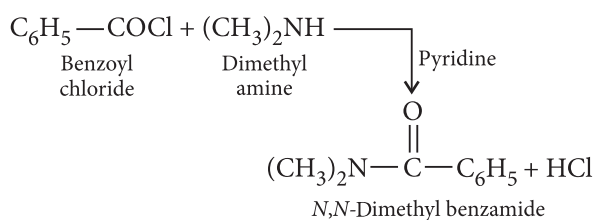
Hence, the reactivity order will be :



OR



4. (a) :



5. (c) : Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM

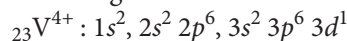
(n = number of unpaired electrons)

Given that, $\mu = 1.73$ BM.

$$\therefore 1.73 = \sqrt{n(n+2)}$$

On solving this equation we get, $n = 1$

So, vanadium atom must have one unpaired electron and thus its configuration is



OR

(b) : Cu^{2+} and Ti^{3+} , both have one unpaired electron.

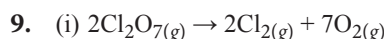
6. (b) : Primary valency corresponds to oxidation number while secondary valency corresponds to coordination number.

7. (a)

OR

(d) : When a copper wire is dipped in silver nitrate solution it turns blue. Cu is more reactive than Ag hence displaces silver from its salt solution.

8. (c) : The aldehydes which have α -H atoms, undergo aldol condensation.



For 1st order reaction,

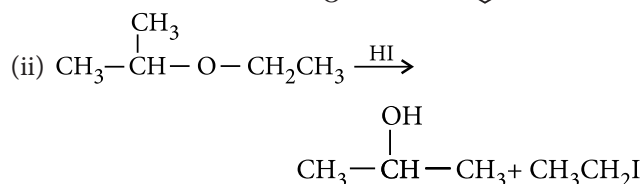
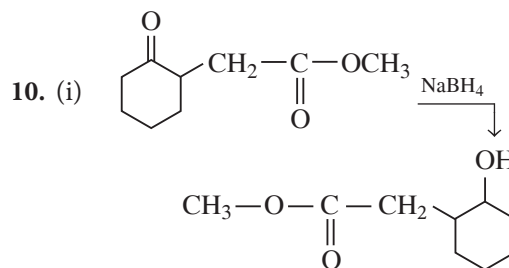
$$k = \frac{2.303}{t} \log\left(\frac{P_0}{P}\right) = \frac{2.303}{55} \log\left(\frac{0.062}{0.044}\right) = 6.2 \times 10^{-3} \text{ s}^{-1}$$

$$(ii) k = \frac{2.303}{t} \log\left(\frac{P_0}{P}\right)$$

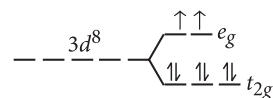
Here $k = 6.2 \times 10^{-3} \text{ s}^{-1}$, $t = 100 \text{ s}$, $P_0 = 0.062 \text{ atm}$

$$\therefore 6.2 \times 10^{-3} = \frac{2.303}{100} \log\left(\frac{0.062}{P}\right)$$

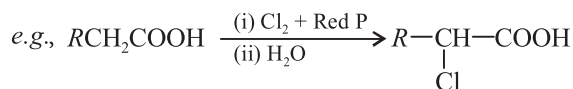
$$\text{or } \log \frac{0.062}{P} = \frac{6.2 \times 10^{-3} \times 100}{2.303} \Rightarrow P = 0.033 \text{ atm}$$



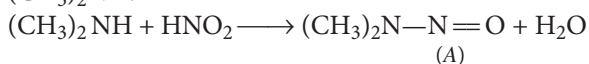
11. (a) Nickel forms octahedral complexes mainly in +2 oxidation state which has $3d^8$ configuration. In presence of strong field ligand also it has two unpaired electrons in e_g orbital.



(b) Carboxylic acids having α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus.



15. (a) The compound A gives a yellow oily substance on treatment with HNO_2 . So, it must be 2°-amine. So, A is $(CH_3)_2NH$.



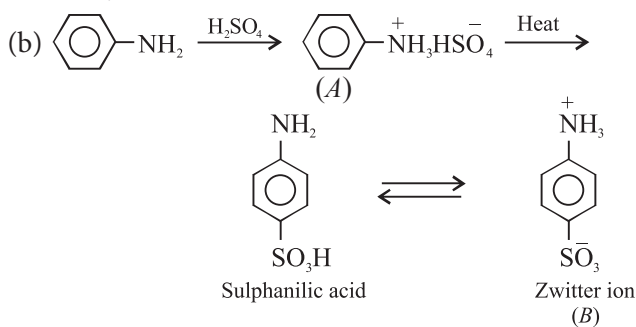
(b) (i) $CH_3-\overset{\substack{| \\ NH_2}}{CH}-CH_3$ is more basic than $CH_3-\overset{\substack{| \\ NH_2}}{CH}-COOCH_3$ because $-COOCH_3$ is an electron withdrawing group which decrease the electron density on nitrogen atom.

(ii) 2° amines are more basic than 1° amines, because in 2° amine there are two electron releasing groups and in 1° amine only one electron releasing group is present, so, $CH_3NHCH_2CH_3$ is more basic than $CH_3CH_2CH_2NH_2$.

(c) (i) In tertiary amines there are no acidic hydrogen due to which they do not undergo acylation reaction.
(ii) N being less electronegative than O gives lone pair of electron more easily than O atom. Therefore, amines are more basic than alcohols.

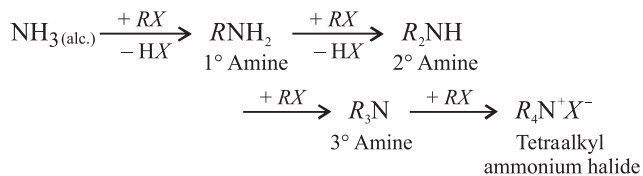
OR

(a) First the mixture is washed with HCl when aniline and *N*-methylaniline are dissolved in it. Then the remaining part is washed with NaOH, when phenol dissolves leaving behind pure toluene. Phenol dissolved in alkali is precipitated by adding HCl. The hydrochloric acid solution of aniline and *N*-methyl aniline is treated first with benzene sulphonyl chloride and then sodium hydroxide. Benzene sulphonyl derivative of aniline dissolves in NaOH. It is filtered off, the filtrate as well as the residue are treated separately first with HCl and then with KOH to obtain pure and *N*-methylaniline separately.



(c) (i) If alkyl halide is in excess, the hydrogen atoms of ammonia are successively replaced by alkyl group to form

primary, secondary and tertiary amines which further react with alkyl halide to form quaternary ammonium salt as follows :



(ii) Both $-NO_2$ and $-COOH$ groups are electron withdrawing groups. They decrease the electron density at the benzene ring and hence deactivate it towards electrophilic substitution reactions.

16. (a) (i) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attractions or metallic bonds. Hence they have high enthalpy of atomization.

(ii) Scandium ($Z=21$) has incompletely filled $3d$ -orbitals in the ground state ($3d^1$). Hence it is considered as a transition element.

(b) The possible oxidation states for $3d^34s^2 = +5, +4, +3, +2$.

The possible oxidation states for $3d^54s^2 = +7, +6, +5, +4, +3, +2$

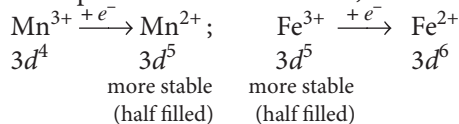
The possible oxidation states for $3d^64s^2 = +6, +4, +3, +2$. In a transition series the oxidation states which lead to exactly half filled or completely filled *d*-orbitals are more stable.

OR

(a) (i) This is due to lanthanoid contraction.

(ii) Much larger third ionisation energy of Mn (where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance and from the relation, $\Delta G^\circ = -nFE^\circ$.

More positive is the value of E° , reaction will be feasible.



Hence, E°_{value} for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+} .

(iii) Manganese can form $p\pi-d\pi$ bond with oxygen by utilising $2p$ -orbital of oxygen and $3d$ -orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi-d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(b) Only those ions will be coloured which have partially filled *d*-orbitals facilitating *d-d* transition. Ions with d^0 and d^{10} will be colourless.

From electronic configuration of the ions, $V^{3+}(3d^2)$ and $Mn^{2+}(3d^5)$ are coloured while $Ti^{4+}(3d^0)$ and $Sc^{3+}(3d^0)$ are colourless.



