CBSE Test Paper-03

Class - 12 Chemistry (Chemical Kinetics)

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1. For the first order reaction, half life is equal to
   a. $\frac{0.693}{K}$
   b. $\frac{2.303[R_o]}{K}$
   c. $\frac{[R_o]}{K}$
   d. $\frac{[R_o]}{2K}$
2. The ionic reactions are generally very fast because
   a. It does not involve bond breaking
   b. The number of collisions between ions are very large
   c. Reactions are highly exothermic
   d. The energy of interaction is between charged ion is greater than between neutral molecules
3. The rate of reaction can be measured as
   a. Rate of reaction can be measured in terms of Rate of disappearance of reactant or rate of appearance of product
   b. Rate of appearance of the product
   c. Rate of appearance of reactant
   d. Rate of disappearance of reactant
4. The rate is independent of the concentration of the reactants in
   a. Zero order
   b. Third order
   c. First order
   d. Second order
5. The half life periods of a reaction at initial concentration 0.1 mol/L and 0.5 mol/L are 200 s and 40 s respectively. The order of the reaction is
   a. 2
   b. $\frac{1}{2}$
   c. 0
   d. 1
6. What is average rate of a reaction? How is it determined?

7. Define - Rate of reaction and the factors affecting the rate of reaction.
8. The reaction $A + B \rightarrow C$ has zero order. What is the rate equation?
9. For the assumed reaction,
   $X_2 + 2Y_2 \rightarrow 2XY_2$
   Write the rate equation in terms of the rate of disappearance of Y_2.
10. Derive the general form of expression of the half life of first order reaction.
11. In the expression of rate of reaction in terms of reactants, what is the significance of negative sign?
12. Show that in case of first order reaction, the time required for 99.9% of the reaction to complete its 10 times that required for half of the reaction to take place.
    (Given: $log2 = 0.3010$)
13. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by Rate = $k[CH_3OCH_3]^{3/2}$. The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,$Rate = k(P_{CH_3OCH_3})^{3/2}$ If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?
14. The following experimental data was collected for the reaction:
    $Cl_2\,(g) + 2NO\,(g) \rightarrow 2NOCl\,(g)$

Trial	**[Cl_2] (mol/L)**	**[NO] (mol/L)**	**Initial Rate, (mol/L/s)**
1	0.10	0.010	1.2×10^{-4}
2	0.10	0.030	10.8×10^{-4}
3	0.20	0.030	21.6×10^{-4}

    Construct the rate equation for the reaction.
15. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

CBSE Test Paper-03

Class - 12 Chemistry (Chemical Kinetics)

Solutions

1. a. $\frac{0.693}{K}$

   Explanation: half life period means the time when concentration of reactant become half to original concentration of reactant.

   for first order reaction rate constant can be calculated as follows:

   $t=\frac{2.303}{k}\log\frac{[A_0]}{[A]}$

   for half life period, $t=t_{1/2}$, $[A]=\frac{[A_0]}{2}$

   on solving,

   $t_{1/2}=\frac{2.303}{k}\log\frac{[A_0]}{\frac{[A_0]}{2}}$

   $t_{1/2}=\frac{2.303}{k}\log 2=\frac{2.303\times 0.3010}{k}$

   $t_{1/2}=\frac{0.693}{k}$

   where letters have their usual meanings.

2. a. It does not involve bond breaking

   Explanation: Ionic reactions does not involve bond breaking. energy is directly used in completing the reaction, therefore they are fast.

3. a. Rate of reaction can be measured in terms of Rate of disappearance of reactant or rate of appearance of product

   Explanation: rate of reaction = (+) rate of appearance of products = (-) rate of disappearance of reactants

4. a. Zero order

   Explanation: $-\frac{d[R]}{d[t]}=k[R]^{\circ}$

5. a. 2

   Explanation: As initial concentration is increased half life is decreasing so order of reaction is 2.

   for second order reaction, $rate\ \alpha\ \frac{1}{[R]}$

6. Average rate of a reaction is defined as the change in concentration of a reactant or a product per unit time. It can be determined by dividing the change in concentration

of reactant or product by the time interval.
For the reaction: $A \rightarrow B$
$R_{av} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$ where R_{av} is the average rate of reaction.

7. The reaction rate for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time. Chemical kinetics of a reaction depend on various factors such as reactant concentrations, temperature, physical states and surface areas of reactants, and also on solvent and catalyst properties if either are present.

8. The rate equation is $Rate = k[A]^0[B]^0$ or Rate = k.

9. Rate of reaction = $-\frac{1}{2}\left[\frac{dY_2}{dt}\right]$

10. For a first order chemical reaction
$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$
$t = t_{1/2}, when [R] = \frac{[R]_0}{2}$
$k = \frac{2.303}{t_{1/2}}\log\left[\frac{[R]_0}{[R]} \times 2\right]$
$k = \frac{2.303}{t_{1/2}}\log 2$
$= \frac{2.303 \times 0.3010}{t_{1/2}}$
$k = \frac{0.693}{t_{1/2}} \Rightarrow t_{1/2} = \frac{0.693}{k}$
Half life period ($t_{1/2}$)is independent of concentration.

11. While writing the expression for rate of a reaction is terms of reactants, the negative sign indicates a decrease in concentration of reactants with time.

12. For a first order reaction
$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$
For 99.9% completion of reaction
$[R]_0$ = 100M, [R] = 100 - 99.9 = 0.1M
$\therefore\ t_{99.99\%} = \frac{2.303}{t}\log\left[\frac{100}{0.1}\right]$ ...(i)
Simiarly, $t_{1/2} = \frac{2.303}{k}\log\left[\frac{100}{50}\right]$ ...(ii)
Divide equation (i) by equation (ii)

$\frac{t_{99.9}}{t_{1/2}} = \frac{\log[1000]}{\log[2]} = \frac{3.0}{0.3010} \approx 10$

Hence $t_{99.9\%}$ = $10t_{1/2}$

13. If pressure is measured in bar and time in minutes, then

Unit of rate = $bar \min^{-1}$

$Rate = k(P_{CH_3OCH_3})^{3/2}$

$k = \frac{Rate}{\left(P_{CH_3OCH_3}\right)^{3/2}}$

Therefore, unit of rate constants$(k) = \frac{bar \min^{-1}}{bar^{3/2}}$

$= bar^{-1/2}\min^{-1}$

14. Let Rate = $k[Cl_2]^x[NO]^y$ where k=rate constant, x and y are orders of reaction w.r.t. X and Y respectively

When Rate = $1.2 \times 10^{-4} mol\ L^{-1} S^{-1}$

$[Cl_2]$ = 0.10 mol/L: [NO] = 0.010 mol/L

$1.2 \times 10^{-4} mol\ L^{-1} S^{-1}$=k[0.10 $molL^{-1}$]x[0.010 mol L^{-1}]^y....(i)

When Rate = $10.8 \times 10^{-4} molL^{-1}s^{-1}$

$[Cl_2]$ = 0.10 mol L^{-1}; [NO] = 0.030 mol L^{-1}

$10.8 \times 10^{-4} = k[0.10 molL^{-1}]^x[0.030 molL^{-1}]^y$.......(ii)

Divide ii by i we get

$9=3^y$ so y=2

When Rate $= 21.6 \times 10^{-4} molL^{-1}S^{-1}$

$[Cl_2]$ = 0.20 mol L^{-1}; [NO] = 0.030 mol L-1

$21.6 \times 10^{-4} = k[0.20 molL^{-1}][0.030 molL^{-1}]^2$....(iii)

Divide iii by ii we get

$2=2^x$ so x=1

Put these values in i we get

$1.2\text{x}10^{-4}$ mol $L^{-1}s^{-1}$=k(0.01 mol/L)(0.01 mol/L)^2

$1.2\text{x}10^{-4}$ mol $L^{-1}s^{-1}$=k$(0.01)^3$ $(mol/L)^3$

k=$1.2\text{x}10^{-4}$ mol $L^{-1}s^{-1}/10^{-6}$ mol^3L^{-3}=120 $mol^{-2}L^2s^{-1}$

So the rate is given as

Rate=120x$[Cl_2][NO]^2$

15. $k = 2.418 \times 10^{-5} s^{-1}$

T= 546 K

$E_a = 179.9 kJmol^{-1} = 179.9 \times 10^3 \, J\, mol^{-1}$

According to the Arrhenius equation,

$k = Ae^{-E_a/RT}$

$\text{Ink} = \text{InA} - \frac{E_a}{RT}$

$\log k = \log A - \frac{E_a}{2.303\, RT}$

$\log A = \log k + \frac{E_a}{2.303\, RT}$

$= \log\left(2.418 \times 10^{-5} s^{-1}\right) + \frac{179.9 \times 10^3 J\, mol^{-1}}{2.303 \times 8.314\, Jk^{-1}\, mol^{-1} \times 546K}$

= (0.3835 - 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

=$3.9 \times 10^{12} s^{-1}$ (approximately)

CBSE Test Paper-02

Class - 12 Chemistry (The d– & f- Block Elements)

1. Silver ornaments turn black by atmospheric
   a. H_2S
   b. O_2
   c. Cl_2
   d. N_2
2. Ni^{2+} in traces can be tested using
   a. Dimethylglyoxime
   b. Potassium ferrocyanide
   c. Ammonium sulphocyanide
   d. Sodium nitroprusside
3. Which one of the following combines with Fe^{2+} ion to form a brown complex?
   a. N_2O_3
   b. N_2O_5
   c. N_2O
   d. NO
4. Which of the following sulphides is soluble in aqua regia?
   a. ZnS
   b. HgS
   c. CdS
   d. HgS , ZnS
5. Among the following, which bivalent ion of the first transition series shows maximum magnetic moment?
   a. Co^{2+}
   b. Ni^{2+}
   c. Mn^{2+}
   d. Fe^{2+}

6. What is the general valence shell configuration of f-block elements?
7. What is the composition of mischmetall? Give its one use.
8. Out of Al, Zn, Mg and Fe which is the maximum density element?
9. Complete the following reactions:
   $CrO_4^{2-} + \_\_\_ \rightleftharpoons \_\_\_ \rightleftharpoons \_\_\_ + H_2O$
10. Why do transition elements show similarities along the horizontal period?
11. Why is any transition series, melting points first increase and then decrease and also they show a dip in the middle?
12. Which is a stronger reducing agent Cr^{2+}or Fe^{2+} and why?
13. Compare the chemistry of actinoids with that of lanthanoids with reference to:
    i. Electronic configuration
    ii. Oxidation states
    iii. Chemical reactivity
14. Write down the electronic configuration of all 3d transition metal atoms. Also show the electronic configuration using electron box diagram.
15. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of oxygen to give compound (B). On heating compound (C) with concentrated H_2SO_4 and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify A to D and also explain the reactions involved.

CBSE Test Paper-02
Class - 12 Chemistry (The d– & f- Block Elements)
Solutions

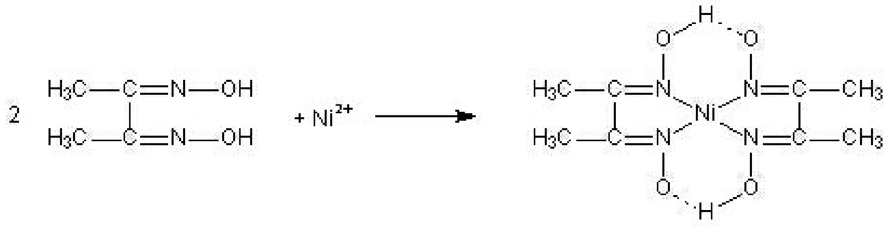
1. a. H_2S

   Explanation: Silver ornaments turns black coming in contact with H_2S due to formation of Ag_2S. The chemical equation for this change can be represented as given below:

   $2Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$

2. a. Dimethylglyoxime

   Explanation: Ni^{2+} forms complex with DMG which is red in colour.



3. d. NO

   Explanation: The brown ring test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution. $[Fe(H_2O)_5NO]^{2+}$ is brown colour complex formed?

   $$NO_3 + 3Fe^{2+} + 4H^+ \rightarrow NO + Fe^{3+} + 2H_2O$$
   $$[Fe(H_2O)]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$

4. b. HgS

   Explanation: HgS is only soluble in aqua regia. Aqua regia is a mixture of concentrated HCl and concentrated HNO_3 in ratio 3:1. The solubilization turns Hg in $HgCl_4^{2-}$, a complex called chloromercurate which is stable in water.

   $3HgS + 2NO_3^- + 12Cl^- + 8H_3O^+ \Leftrightarrow 3HgCl_4^{2-} + 2NO + 12H_2O + 3S$

5. c. Mn^{2+}

Explanation: Mn^{2+} has d^5 configuration so maximum number of unpaired electrons and hence maxium magnetic moment. This magnetic moment can be calculated by using the spin only formula: $\mu_{so} = \angle n(n+2)$, where n= number of unpaired electrons.

6. F-block elements are those in which the last electron enters the f orbital. F- orbital can accommodate maximum of 14 electrons.
   The general electronic configuration of f-block elements is
   $(n-2)\ f^{1-14}(n-1)\ d^{0-1}ns^2$
7. Mischmetall is an alloy which consists of a Lanthanoid metal (95%) and iron(5%) and traces of S, C, Ca & Al. A good amount of this alloy is used in magnesium based alloy to produce bullets, shell and lighter Flint.
8. Fe
9. $2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$
10. There are greater horizontal similarities in the properties of then transition elements in contrast to the main group elements.This is because all of them contain incompletely filled d-subshell in ground state or in stable oxidation state.
11. Melting points first increase because the number of unpaired electrons increases. Due to increase in the number of unpaired electron, strength of metallic bonding increases and hence melting point increases. After reaching the maximum, the melting points decrease because the pairing of electrons starts in the d-subshell and number of unpaired electrons decreases and so the strength of metallic bond decreases. The dip in the middle is due to exactly half filled configuration of d-subshell (d^5)which has higher stability. Hence, electrons are held tightly by the nucleus. As a result, metallic bond is weaker. And thus melting point graph shows dip at this point.
12. Reducing agents are those which itself get oxidised and make the other substance get reduced. The following reactions are involved when $Cr^{2+}$and Fe^{2+}act as reducing agents.
    $Cr^{2+} \rightarrow Cr^{3+} + e^-$ and $Fe^{2+} \rightarrow Fe^{3+} + e^-$. The $E^\circ_{Cr^{3+}/Cr^{2+}}$ value is - 0.41 V and $E^\circ_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+}can be easily oxidized to $Cr^{3+}, but\ Fe^{2+}$does not get oxidized to Fe^{3+}easily. Therefore, $Cr^{2+}$is a better reducing agent than Fe^{3+}.
13. i. **Electronic configuration :** In lanthanoids 4f - orbitals are progressively filled so

their electronic configuration is $4f^{1\text{-}14}\ 5d^{0\text{-}1}\ 6s^2$ whereas in actinoids 5f-orbitals are progressively filled so their electronic configuration is $5f^{1\text{-}14}6d^{0\text{-}1}\ 7s^2$

ii. **Oxidation states:** Lanthanoid show +3 oxidation state. Some elements show +2 and +4 oxidation states also. Actinoids show +2 ,+4, +5, +6, + 7 oxidation states. Although +3 and +4 are most common.

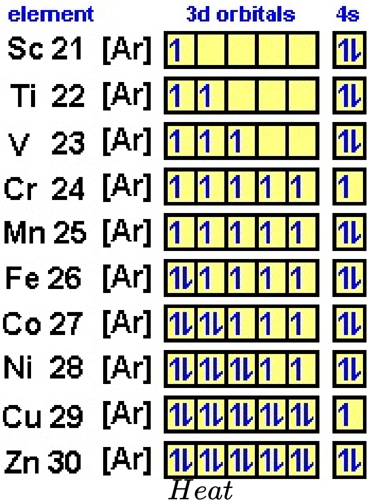
iii. **Chemical reactivity:** Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionization energy.

14. Electronic configuration of 3d metal atoms is as follows:

Sc(Z=21) : $[Ar]3d^14s^2$, Ti(Z=22) : $[Ar]3d^24s^2$, V(Z=23) : $[Ar]3d^34s^2$,Cr(Z=24) : $[Ar]3d^54s^1$, Mn(Z=25) : $[Ar]3d^54s^2$

Fe(Z=26) : $[Ar]3d^64s^2$, Co(Z=27) : $[Ar]3d^74s^2$, Ni(Z=28) : $[Ar]3d^84s^2$, Cu(Z=29) : $[Ar]3d^{10}4s^1$, Zn(Z=30) : $[Ar]3d^{10}4s^2$

Electron box diagram is shown below:



element		3d orbitals					4s
Sc 21	[Ar]	↑					↑↓
Ti 22	[Ar]	↑	↑				↑↓
V 23	[Ar]	↑	↑	↑			↑↓
Cr 24	[Ar]	↑	↑	↑	↑	↑	↑
Mn 25	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe 26	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co 27	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni 28	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu 29	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn 30	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

15.
$$\underset{(A)}{KMnO_4} \xrightarrow{Heat} \underset{(B)}{K_2MnO_4} + \underset{(C)}{MnO_2} + O_2$$
$$MnO_2 + KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$MnO_2 + 4NaCl + 4H_2SO_4 \rightarrow \underset{(D)}{MnCl_2} + 2NaHSO_4 + Cl_2 + H_2O$$

From the above set of reaction we can deduce that:

(A) = $KMnO_4$

(B) = K_2MnO_4

(C) = MnO_2

(D) = $MnCl_2$

CBSE Test Paper-03

Class - 12 Chemistry (The d– & f- Block Elements)

1. Transition metals with highest melting point is
   a. Hg
   b. Sc
   c. Cr
   d. W
2. Which of the following is not considered a transition metal?
   a. Zn
   b. Ac
   c. Y
   d. La
3. Which is the most stable oxidation state of iron?
   a. +1
   b. +3
   c. 0
   d. +2
4. In the reaction, $SnCl_2 + HgCl_2 \rightarrow A + SnCl_4$, A is
   a. $HgCl_2$
   b. Hg
   c. HgCl
   d. $HgCl_3$
5. Maximum magnetic moment is shown by
   a. d^6
   b. d^8
   c. d^7
   d. d^5
6. Write the outer electronic configuration of Lanthanoids.
7. Name the lanthanoid element which exhibit +4 oxidation state besides +3 oxidation

state.

8. Name the transition element which does not exhibit variable oxidation states.

9. Why do actinoids, in general, exhibit a greater range of oxidation states than the lanthanoids?

10. Why are Fe^{2+} compounds easily oxidises to Fe^{3+} as compared to Mn^{+2} compounds.

11. Explain why
    i. E^{o} for Mn^{3+}/Mn^{2+} couple is more positive than that for Fe^{3+}/Fe^{2+} (At. No. of Mn= 25, Fe = 26)
    ii. Ce^{3+} can be easily oxidized to Ce^{4+} (At. No. of Ce = 58)

12. Uses Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin only' formula.

13. What are alloys? Name an important alloy which contains some of the Lanthanoid metals. Mention its uses.

14. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statements by giving some examples from the oxidation state of these elements.

15. Indicate the steps in the preparation of:
    i. $K_2Cr_2O_7$ from chromite ore.
    ii. $KMnO_4$ from pyrolusite ore.

CBSE Test Paper-03

Class - 12 Chemistry (The d– & f- Block Elements)

Solutions

1. d. W

   Explanation: The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)d in addition to the ns electrons in the interatomic metallic bonding. W belongs to 5d series and it has lot of unpaired electrons ($5d^4 6s^2$).

2. a. Zn

   Explanation: Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the three transition series, their chemistry is studied along with the chemistry of the transition metals.

3. b. +3

   Explanation: Fe has d^5 configuration in +3 oxidation state.

4. b. Hg

   Explanation: Tin(II) chloride react with mercury(II) chloride in acidic medium to produce mercury and tin(IV) chloride as given below:

   $SnCl_2 + HgCl_2 \rightarrow Hg + SnCl_4$

5. d. d^5

   Explanation: Magnetic moment is directly proportional to the total number of unpaired electrons. So it will be maximum for the element having maximum unpaired electrons i.e. d^5 system.

6. $4f^{1\text{-}14}5d^{0\text{-}1}6s^2$ is outer electronic configuration of Lanthanoids.

7. Generally, Lanthanide elements shows +3 oxidation state but cerium apart from +3 shows +4 oxidation state. The formation of Ce(IV) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E^o

value for Ce^{4+}/ Ce^{3+} is + 1.74 V.

8. Scandium (Z= 21) does not exhibit variable oxidation states. It shows only +3 oxidation state.
9. They have lower ionization energy and less effective nuclear charge therefore more number of valence electrons can take part in bond formation. Also there is very less difference between the enegry of 5f ,6d,7s orbitals.
10. Mn^{2+} compounds are less readily converted to its +3 oxidation state (Mn^{3+}) as compared to Fe^{2+} because Mn^{2+} ($3d^5$) is more stable than Mn^{3+} ($3d^4$) due to stable half filled d-orbital electronic configuration. Whereas Fe^{3+} ($3d^5$) is more stable than Fe^{2+} ($3d^6$) due to half filled d-orbitals therefore Fe^{2+} gets easily converted to Fe^{3+}
11. i. Mn^{2+} is more stable($3d^5 4s^0$) because of half filled d-orbitals than Mn^{3+}($3d^4 4s^0$) whereas Fe^{3+}($3d^5$ $4s^0$) is more stable than Fe^{2+}($3d^6 4s^0$), therefore Mn^{3+} can be easily reduced to Mn^{2+} whereas Fe^{3+} is not easily reduced to Fe^{2+} rather Fe^{2+} is more easily oxidized to Fe^{3+}.
    ii. Ce^{4+} is more stable than Ce^{3+} because of stable inert gas configuration and higher hydration energy hence Ce^{3+} is easily oxidized to Ce^{4+}.
12. $_{58}Ce$ has electronic configuration as $[Xe]^{54}$ $4f^1$ $5d^1$ $6s^2$ while Ce^{3+} will have electronic configuration as $[Xe]^{54}$ $4f^1$.
    Thus, number of unpaired electron in Ce^{3+} is 1. $\mu = \sqrt{n(n+2)}$
    $= \sqrt{1(1+2)} = \sqrt{3}BM$
    = 1.73 BM
13. Alloys are homogenous mixture of two or more metals. One of them can be non metal also. Mischmetal is an alloy which contains some of the Lanthanoid metals, it contains 45% Lanthanoid metals and iron ~ 5% and traces of S, C, Ca and Al.
    Mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint.
    Addition of 3% mischmetal to magnesium increases its strength and used in making jet engine parts.

14. Chemistry of actinoids is not as smooth as lanthanoids because actinoids are radioactive elements and they show a large number of oxidation state compared to lanthanoids. Lanthanoids shows limited number of oxidation state like + 2,+3 and +4 (out of which +3 is most common). This is because of large energy gap between 4f, 5d and 6s subshells. The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation state also e.g. uranium (Z= 92) and plutonium (Z= 94) show +3, +4, +5 and +6 neptunium (Z = 94) shows +3, +4, +5 and +7 etc This is due to small energy difference between 5f, 6d and 7s subshells of the actinoids.

15. i. Potassium dichromate $(K_2Cr_2O_7)$ is prepared from chromite ore $(FeCr_2O_4)$ in the following steps.

Step (1): Preparation of sodium chromate- Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or

potassium carbonate in free access of air.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Step (2): Conversion of sodium chromate into sodium dichromate- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7$. $2H_2O$ can be crystallised. $2Na_2CrO_4 + conc.\,H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Step(3): Conversion of sodium dichromate to potassium dichromate- Sodium dichromate is more soluble than potassium dichromate, therefore it is prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$2\ CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{\ 2-} + H_2O$

$Cr_2O_7^{\ 2-} + 2\ OH^- \rightarrow 2\ CrO_4^{\ 2-} + H_2O$

The combined reaction can be shown like:

$$\underset{\substack{Chromate\\(Yellow)}}{2CrO_4^{2-}} \underset{Alkali}{\overset{Acid}{\longleftrightarrow}} \underset{\substack{Hydrogen\\chromate}}{2HCrO_4^-} \underset{Alkali}{\overset{Acid}{\longleftrightarrow}} \underset{\substack{Dichromate\\(Orange)}}{Cr_2O_7^{2-}}$$

ii. Potassium permanganate $(KMnO_4)$ can be prepared from pyrolusite.(MnO_2) The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO_3 or $KClO_4$ to give K_2MnO_4

$$2MnO_2 + 4KOH + O_2 \xrightarrow{heat} \underset{(Green)}{2K_2MnO_4} + 2H_2O$$

This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (Vl).

$$MnO_2 \xrightarrow{fused\ with\ KOH\ and\ oxidised\ by\ KNO_3\ or\ air} MnO_4^{2-}$$

$$MnO_4^{2-} \xrightarrow{electrolytic\ oxidation\ in\ alkaline\ solution} MnO_4^-$$

In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$