CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE, BACHELOR OF SCIENCE IN CHEMISTRY AND BACHELOR OF SCIENCE IN INDUSTRIAL CHEMISTRY

CHEM 419: CHEMISTRY OF TRANSITION ELEMENTS

STREAMS: BSC , BSc. CHEM, BSc Industrial Chem (Y4S1) **TIME: 2 HOURS**

DAY/DATE: TUESDAY 19/12/2023 **11.30 A.M. – 1.30 P.M.**

INSTRUCTIONS:

- Answer Question ONE and Any other TWO Questions

QUESTION ONE. (30 marks)

(a). (i). Explain the position and classification of the transition elements in the periodic table and give reasons why they are called transition elements **[3marks]**

(ii) Explain why transition elements tend to form large number of complexes. **[3 marks]**

(b) (i). Enumerate the characteristics of transition elements. **[5 marks]**

(ii) Which of the d block elements may not be regarded as transition elements. Give reasons for your answer **[3 marks]**

(c)(i). Explain the metallic character of the d-block elements. Why are Cr, Mo and W hard metals with high melting and boiling points while Zn, Cd and Hg

are soft with low melting and boiling points **[3 marks]**

(ii). Discuss the oxidation states of the first row transition elements and give reasons why the highest oxidation state of a transition metal is exhibited in its oxide or fluoride? **[3 marks]**

d) List the first row transition metals in the ascending order of atomic numbers and hence answer the following questions. Give reasons for your answers **[5 marks]**

(i) Write the element which shows maximum number of oxidation states
(ii) Which element has the highest melting point?
(iii) Which element shows only +3 oxidation state?
(iv) Which element is a strong oxidising agent in +3 oxidation state
(v) There is hardly any increase in atomic size with increasing atomic numbers in the above series of transition metals. Discuss

(e) (i).Write the expected and the observed electronic configuration beyond the inert gas core of the following elements belonging to first row transition series Mn, Cr and Ni. Give reasons for any irregularities from the expected electronic configuration **[3 marks]**

(ii) Write the electronic configuration beyond the inert gas core of the following ions. Predict which of the ions will be coloured in aqueous solutions. Give reasons for your answer
I. V^{5+}, II Cr^{3+}, III Mn^{2+}, IV Cu^{2+} V Sc^{3+} VI Ti^{4+} **[3 marks]**

QUESTION TWO (20 marks)

(a). (i). Define the term ionization enthalpy **[2 marks]**

(ii). Explain the trends observed in the ionization enthalpies of the d-block elements. How would you account for the irregular variation of the first and

second ionization enthalpies in the first series of transition elements? **[3 marks]**

(b) (i). Define the following: (i) diamagnetic, (ii) paramagnetic and (iii) ferromagnetic compounds. **[3 marks]**

(ii). Explain the origin of the magnetic moments for transition metal compounds and derive spin only formula for calculating magnetic moments and the unpaired electrons in a transition metal compound**(3 marks)**.

(iii). Why does Mn(II) ion show maximum paramagnetic character amongst bivalent ions of the elements of the 3d series **[2.marks]**

(iv). Calculate the spin only magnetic moment of M^{2+} (Z= 28) **(2 marks)**

(c). Give reasons why many of the transition metals and their compounds act as catalysts **[3 marks]**

(d). By giving an example, suggest reasons for the following features of the transition elements "The lowest oxides of transition metal are basic, the highest are amphoteric/acidic' **[2 marks]**

QUESTION THREE (20 marks)

(a).(i)The elements of the first transition series are much important than those of the second and third series. Their chemistry is best considered separately. Give reasons for this assertion **[3 marks]**

(b).(i).Distinguish between interstitial compounds and alloy. Give an example of each and explain why such compounds are well known in transition metals **[3 marks]**

(ii) Give any four characteristics of interstitial compounds **[2 marks]**

(c) (i) What is meant by the term disproportionation? [Hint: Use the following

two reactions below as examples to illustrate your explanation **[2 marks]**

(i). $3CrO_4^{3-} + 8H^+ \longrightarrow 2CrO_4^{2-} + Cr^{3+} + 4H_2O$

(ii) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^{-} + MnO_2 + 2H_2O$

(ii) Distinguish between standard reduction potential and standard oxidation potential. Explain how they are measured and comment on their relationship **[3 marks]**

(d)(i). Discuss briefly the reducing and oxidizing ability of chemical species in aqueous solution on the basis of reduction potential **[3 marks]**

(ii). For M^2 /M and M^{3+} /M^{2+} systems the E^O values for some metals are as follows

M^{2+}/M	E^0	M^{3+}/M^{2+}	M^0
Cr^{2+}/Cr	−0.9V	Cr^{3+} /Cr^2	−0.4V
Mn^{2+}/Mn	−1.2V	Mn^{3+}/Mn^{2+}	+1.5V
Fe^{2+}/Fe	−0.4V	Fe^{3+} /Fe^{2+}	+0.8V

Use the above data to comment on

(i). The relative stability of the Cr^3, Fe^3 and Mn^{3+} **(2 marks)**

(ii). The ease with which Fe can be oxidized as compared to a similar process for either Cr or Mn **[2 marks]**

QUESTION FOUR [20 marks]

a).(i).Enumerate the main differences between the second and third series of transition elements on one hand and those of the first series of transition elements on the other hand with respect to **any THREE** of the following

(4.5 marks)

(i). Electronic configuration

(ii). Atomic and ionic radii sizes

(iii). Oxidation states

(iv). Formation of metal–metal bonds

(v). Magnetic properties

(vi). Ligand —donor prevalence and coordination number

b). (i) What are inner transition elements? **(1.5 marks)**

(ii). Describe properties which demonstrate that f block elements are different from d-block elements **[4.5 marks]**

(c). Give brief explanation to the following

(i) Metal–metal bonding is more frequent for the 4*d* and the 5*d* series of transition metal than that for the 3*d* series. **[2 marks]**

(ii).The atomic radii of the metals of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second (4*d*) series. **[2 marks]**

(c). Explain by comparing and contrasting the oxidation states of actinides and lanthanides and explain why actinide elements show larger number of oxidation states than lanthanides? **[2.5marks]**

(f). Account for the ***ANY TWO*** of the following observations **(3 marks)**

(i). Although Cr^{6+} complexes do exist, they are usually powerful oxidizing agents, whereas $Mo^{6+}$and W^{6+} are quite stable

(ii). Among the lanthanides, Ce^{3+} is easily oxidized and forms tetra positive Ion Ce^{4+}in aqueous solution which is used as an oxidizing agent in volumetric analysis.

(iii). Lanthanum, gadolinium and lutetium show different configuration and oxidation states

(iv). Of the d^4 species, Cr (II) is strongly reducing while Mn (III) is strongly oxidizing

(v). Transition metals have high densities and high melting and boiling points

QUESTION FIVE. (20 marks)

a) (i).State the features of electronic configuration for lanthanides.**[2 marks]**

(ii).What are different oxidation states exhibited by lanthanides? Explain why Eu and Yb show +2 oxidation state **[2 marks]**

b). Compare the chemistry of lanthanides with that of actinides with special reference to **[5marksl**

i. Electronic configuration
ii. Atomic and ionic sizes Oxidation state
iii. Chemical reactivity
iv. Tendency to form complexes

c) (i) Distinguish between lanthanide contraction and actinide contraction.

(ii). Explain why actinide contraction is more than lanthanide contraction **[2 marks]**

(iii). What are the causes and consequences of lanthanide contraction? **[3.5 marks]**

(d) Briefly explain the following

i. Although the common oxidation state of lanthanide elements is $+3$, the $+2$ oxidation state of Eu and Yb is significant **[2 marks]**

ii. Ce^{4+} and Tb^{4+} are more stable with respect to reduction than other Ln^{4+} cations while Eu^{2+} and Yb^{2+} are more stable with respect to oxidation than any other Ln^{2+} cations **[2 marks]**

iii. Unlike CeF_4, $CeCl_4$ does not exist, though $CeCl_3$ does exist **[1.5 marks]**

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