University of Fort Hare
Together in Excellence

PAC 123 F

Degree Examinations: November 2017

Subject: DESCRIPTIVE CHEMISTRY

Time: 3 hours **Marks: 100**

This question paper consists of SEVEN pages

ANSWER ALL QUESTIONS

Each question carries 25 marks

ALL COMPUTATIONS MUST BE ROUNDED-OFF TO THE CORRECT NUMBER OF SIGNIFICANT FIGURES

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Question 1
Spontaneity, Entropy & Free Energy

1. The element cesium (Cs) freezes at 28.4 ° C, and its molar enthalpy of fusion is ΔH_{fus} = 2.09 kJ/mol.
   a. When liquid cesium solidifies to Cs (s) at its normal melting point, is ΔS positive or negative?
   b. Calculate the value of ΔS when 1.00 mol of Cs solidifies at 28.4 ° C. [5]

2. Hydrogen cyanide is produced industrially by the following exothermic reaction

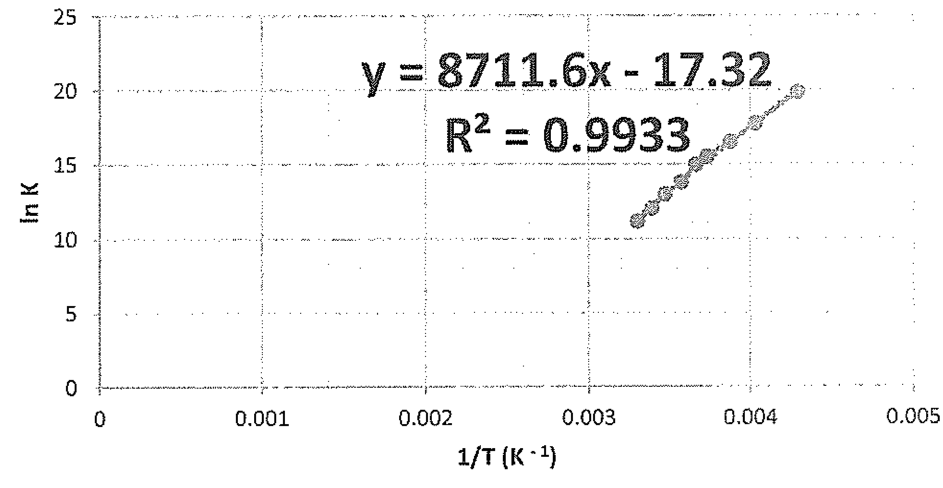
$$2NH_3\,(g) + 3O_2\,(g) + 2CH_4\,(g) \xrightarrow[\text{Pt - Rh}]{1000\,^\circ C} 2HCN\,(g) + 6H_2O\,(g)$$

   Is the high temperature needed for thermodynamic or kinetic reasons? [4]

3. For a certain chemical reaction, $\Delta H°$ = 19.5 kJ, and $\Delta S°$ = 42.7 J/K.
   a. Is the reaction exothermic or endothermic?
   b. Does the reaction lead to an increase or decrease in the disorder of the system?
   c. Calculate $\Delta G°$ for the reaction at 298 K
   d. Is this reaction spontaneous at 298 K? [5]

4. Use the following plot to determine $\Delta H°$ and $\Delta S°$ for the following process.

$$2ClO\,(g) \rightleftharpoons Cl_2O_2\,(g)$$



   At what temperatures is this reaction spontaneous? [5]

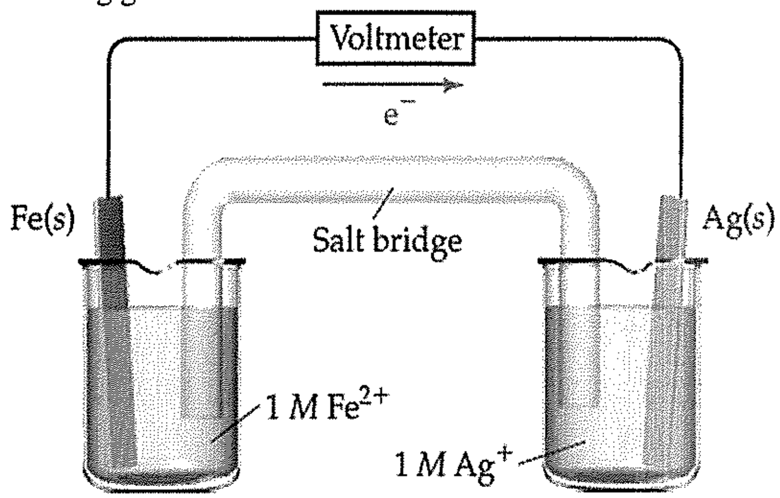
5. If wet silver carbonate is dried in a stream of hot air, the air must have a certain concentration level of carbon dioxide to prevent silver carbonate from decomposing by the reaction

$$Ag_2CO_3\,(s) \rightleftharpoons Ag_2O\,(s) + CO_2\,(g)$$

   $\Delta H°$ for this reaction is 79.14 kJ/mol in the temperature range of 25 to 125 ° C. Given that the partial pressure of carbon dioxide in equilibrium with pure Ag_2CO_3 is 6.23 x 10^{-3} torr at 25 ° C, calculate the partial pressure of CO_2 necessary to prevent decomposition of Ag_2CO_3 at 110 ° C. [6]

Question 2
Electrochemistry

1. Consider the following galvanic cell:



Give the balanced cell reaction, the standard line notation, and determine E^o_{cell}. [5]

2. The standard electrode potentials at 298 K for $Ni^{2+}(aq) \mid Ni(s)$ and $Hg^{2+}(aq) \mid Hg(\ell)$ are –0.25 and 0.85 V, respectively. Calculate the equilibrium constant at 298 K for the reaction

$$Ni^{2+}(aq) + Hg(\ell) \rightarrow Ni(s) + Hg^{2+}(aq)$$

[5]

3. Magnesium metal is used as a sacrificial anode to protect underground pipes from corrosion. Why is magnesium metal referred to as a "sacrificial anode"? Using the given Table, suggest what metal the underground pipes could be made from in order for magnesium to be successful as a sacrificial anode. [4]

4.
   a. What is electrolysis?
   b. Are electrolysis reactions thermodynamically spontaneous?
   c. What are the expected half reactions at each electrode in the electrolysis of molten $AlBr_3$?
   d. Give a balanced reaction for the electrolysis of molten $AlBr_3$ [6]

5. How many hours will it take to deposit 35.3 g of Cr from a solution of $Cr_2(SO_4)_3$ at a current of 6.00 A? [5]

Question 3
Representative Elements

1. The electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. Write the balanced equations for the electrolysis of brine (hydrogen gas is also produced) and for the electrolysis of molten sodium chloride. [5]

2. Each of the following compounds is a basic, acidic, or amphoteric oxide:
   a. MgO b. Al_2O_3
   For each substance write the equation for the reaction with water, and if possible, with an acid or base. [4]

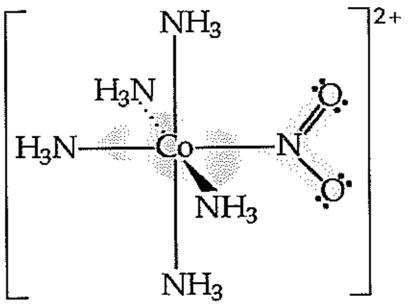
3. Calculate the pH of a 0.050 M $Al(NO_3)_3$ solution The K_a value for $Al(H_2O)_6{}^{3+}$ is 1.4 x 10^{-5}. [5]

4. Write the Lewis structure of each of the following species, and predict the molecular structure of each
   a. $SeO_3{}^{2-}$
   b. S_2Cl_2
   What is the hybridization of the central atom in each case? [6]

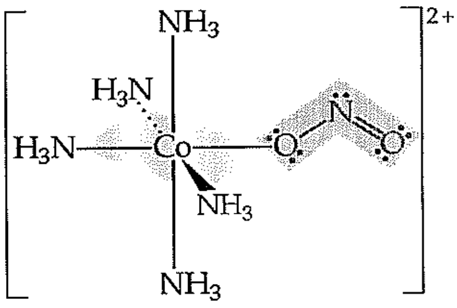
5. For the molecule XeO_2F_2, write Lewis structure, predict the molecular structure (including bond angles), and give the expected hybridization of the central atom. [5]

Question 4
Transition Elements and Coordination Compounds

1. What type of isomers are depicted in the following diagram



(a)

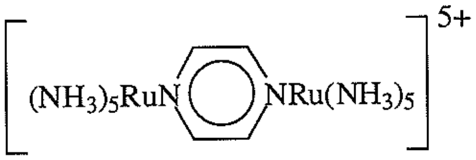


(b)

Name these complex ions. [4]

2. The $Co(NH_3)_6\,^{3+}$ ion is diamagnetic, but $Fe(H_2O)_6\,^{2+}$ is paramagnetic. Explain. [6]

3. One of the most famous species in coordination chemistry is the Creutz-Taube complex,



It is named after the two scientists who discovered it and initially studied its properties. The central ligand is pyrazine, a planar six-membered ring with nitrogen at opposite sides.

   a. How can you account for the fact that the complex, which has only neutral ligands, has an odd overall charge?
   b. The metal is in low-spin configurations in both cases. Assuming octahedral coordination, draw the *d*-orbital energy-level diagram for each metal.
   c. In many experiments, the two metal ions appear to be in exactly equivalent states. Can you think of a reason that this might appear to be so, recognizing that the electrons move rapidly compared to nuclei? [6]

4. What is lanthanide contraction? How does the lanthanide contraction affect the properties of the 4d and 5d transition metals? [4]

5. Pb is recovered from its ore galena (PbS) by roasting of PbS with O_2 to form PbO_2 followed by reduction with carbon to form CO_2 and metallic Pb. Write the balanced equations for both these steps. [5]

PERIODIC TABLE OF ELEMENTS

1 1A Alkali metals	2 2A Alkaline earth metals	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A Halogens	18 8A Noble gases
					Transition metals												
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 35.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac** (227)	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						

metals ← → nonmetals

* Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
** Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Important constants

$$R = 8.314\ \mathrm{J/mol\cdot K} = 0.08206\ \mathrm{L\cdot atm/mol\cdot K}$$

$$F = 96485\ \mathrm{C/mol}$$

Important Formulas

$$\Delta G^o = -RT\ln K$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$E^o_{cell} = [E^o(\text{cathode}) - E^o(\text{anode})]$$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln(Q)$$

$$m = \frac{tIM}{nF}$$

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}°$ (V)	Half-Reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		