M.Sc. CHEMISTRY
First Semester
ANALYTICAL CHEMISTRY
(MSC - 101)

Duration: 3Hrs.   **Full Marks: 70**

Part-A (Objective) =20
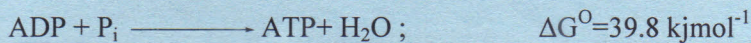Part-B (Descriptive) =50

(PART-B: Descriptive)

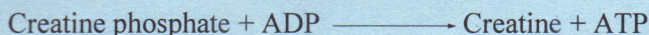**Duration: 2 hrs. 40 mins.**   **Marks: 50**

Answer any *four* from *Question no*. 2 to 8
Question no. 1 is compulsory.

1. (a) Define equivalent mass of an oxidizing agent.   (2)

   (b) The value of ΔG^O for the following reactions are given.   (2)

   Creatine phosphate + H_2O $\longrightarrow$ Creatine + P_i; ΔG^O= -43.5 kjmol^{-1}

   ADP + P_i $\longrightarrow$ ATP+ H_2O ; ΔG^O=39.8 kjmol^{-1}

   Calculate the $\Delta G^O{}_{net}$ for the following reaction-

   Creatine phosphate + ADP $\longrightarrow$ Creatine + ATP

   (c) Draw the TGA plot for hydrated calcium oxalate.   (2)

   (d) Calculate the results of the following expression: (2)

   $(21.3\pm0.1)(17.6\pm0.02)$

   (e) Write briefly about the classification of analytical methods.   (2)

2. (a) What do you mean by a standard solution? Explain with example what a

   primary standard is and what a secondary standard is.   (3)

   (b) Calculate the number of mmoles contained in 300 mg of an organic compound

   of molecular formula $C_7H_6O_2$.   (2)

   (c) (i) Calculate the molar concentration of $NO_3{}^-$ ion in a solution prepared by

   mixing 200 mL of 0.25 M KNO_3 and 300 mL of 0.20 M $Ca(NO_3)_2$ solution.

   [$NO_3{}^{-1}$ = 62 gmol^{-1}]   (3)

(ii) What is the pc weight of Ag in 8.4g sample of AgCl of 80% purity? (Atomic mass of $1Ag=108g/mol$) (2)

3. (a) Two sets of results in mg/Lit; One obtained by a standard method and other by a new method are given below: (5)

Standard method: 30 25 22 23 35 31 33

New method: 25 26 28 30 24 28 22

Determine whether precision of new method differs significantly from that of standard method or not. The critical value of F for 7 degrees of freedom is 1.56.

(b) Write three differences between accuracy and precision. (3)

(c) What is confidence limit? Give mathematical expression for it. (2)

4. (a) How can you predict the following stages of a reaction by comparing the value of K_c and Q_c when- (3)

(i) Net reaction proceed in forward direction.

(ii) Net reaction proceed in backward direction.

(iii) No net reaction occurs.

(b) Match column I with column II. (5)

Column I	Column II
(i) Equilibrium	(a) $\Delta G>0$, $K<1$
(ii) Spontaneous	(b) $\Delta G=0$
(iii) Nonspontaneous	(c) $\Delta G^\circ=0$
	(d) $\Delta G<0$, $K>1$

(c) Write the relationship between Solubility (S) and K_{SP} for the electrolyte $Ca_3(PO_4)_2$. (2)

5. (a) Explain the principle and instrumentation in Differential Thermal Analysis. (5)

(b) Draw and explain the DTA curve for Sulphur. (5)

6. (a) An acidified solution of Fe^{+2} is titrated with 0.03 (M) $KMnO_4$ solution. If the titration required 22.4 mL, how many mg of Fe^{+2} are in solution? (at mass of Fe = 55.8 g/mole) (3)

(b) Calculate the normality of a Na_2CO_3 solution containing 1.06 g Na_2CO_3 in 200 mL (2)

(c) Write about determinate errors and indeterminate errors. (including all classification) (5)

7. (a) Mention the instrumentation involved in Inductively Coupled Plasma – Atomic Emission Spectroscopy. (5)

(b) (i) What will happen to the number of moles of SO_3 in equilibrium with SO_2 and O_2 in each of the following cases in the reaction? (2+3=5)

$$2SO_3 (g) \rightleftharpoons 2SO_2 (g) + O_2 (g) ; \Delta H^\circ = 197 \text{ kJ}$$

a. Oxygen gas is added

b. The pressure is increased by decreasing the volume of the reaction container.

c. The temperature is decreased.

d. Gaseous sulfur dioxide is removed.

(ii) Mention the conditions required for getting favorable yield of ammonia in Haber process.

8. (a) What do you understand by quantitative and qualitative analysis? Write briefly about gravimetric and volumetric analysis. (6)

(b) Write briefly about the decomposition and dissolution of the samples. (4)

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Duration: 20 minutes   **Marks – 20**

(PART A - Objective Type)

I. Choose the correct answer: **1×20=20**

1. Normality of 1.72 g/L a solution of $Ba(OH)_2$, [molar mass 172 gmol^{-1}], is
   (i) 0.01(N)   (ii) 0.02(N)   (iii) 0.2 (N)   (iv) 0.1 (N)

2. Number of mmol in 29.8 mg of KCl, [mol mass 74.5 gmol^{-1}], is
   (i) 0.10   (ii) 0.20   (iii) 0.40   (iv) 0.04

3. The ppm concentration of 2.50×10^{-4} M Mg^{2+} [atomic mass 24 gmol^{-1}], is
   (i) 1.6   (ii) 6.0   (iii) 60.0   (iv) 10.0

4. If molar mass of $K_2Cr_2O_7$ is M gmol^{-1}, its equivalent weight in acidic medium is
   (i) M/6   (ii) M/3   (iii) M/5   (iv) M

5. Identify the **INCORRECT** statement regarding chemical equilibrium
   (i) All chemical reactions are, in principle, reversible.
   (ii) Equilibrium is achieved when the forward reaction rate equals the reverse reaction rate.
   (iii) Equilibrium is achieved when the concentration of species become constant.
   (iv) Equilibrium is achieved when the reaction quotient Q equals the equilibrium constant.

6. Consider the gas-phase equilibrium system represented by the equation:
   $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$
   Given that the forward reaction (the conversion of "left-hand" species to "right-hand" species) is **endothermic**, which of the following changes will **decrease** the equilibrium amount of H_2O?
   (i) Adding more oxygen.
   (ii) Adding a solid phase catalyst.
   (iii) Decreasing the volume of the container (the total pressure increases).
   (iv) Increasing the temperature at constant pressure.

7. For the reaction:
   $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$;
   The standard free energy change is greater than zero. The probable value of equilibrium constant for this reaction may be-
   (i) K=0   (ii) K>1   (iii) K<1   (iv) K=1

8. In which of the following reaction, the equilibrium remains unaffected on addition of small amount of small amount of argon at constant volume-
   (i) $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$ (ii) $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$
   (iii) $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ (iv) The equilibrium will unaffected in all the three cases.

9. In ICP-AES the gas used to create the plasma
   (i) Hydrogen   (ii) Argon
   (iii) Krypton   (iv) Neon

10. DSC measures physical properties of a sample change along with-
   (i) Concentration against absorbance   (ii) Heat flow against temperature
   (iii) Temperature against time   (iv) Pressure against volume

11. In AAS the cathode lamp is filled with
   (i) CO_2 (ii) O_2 (iii) Ne   (iv) SO_2

12. In TGA instrument the sample is heated up to
   (i) $1500\ ^0C$ (ii) 2000^0C (iii) $3500\ ^0C$ (iv) $4000\ ^0C$

13. The precision cannot be expressed by
   (i) Average deviation from the mean   (iii) Standard deviation
   (ii) Relative Standard deviation   (iv) Absolute error

14. If Relative Standard deviation (RSD) is expressed in terms of per cent, then obtained RSD is called
   (i) Coefficient of variation   (iii) Absolute error
   (ii) Gross error   (iv) None of these

15. The determinate errors which cannot be corrected easily is
   (i) Instrument error   (ii) Method error
   (iii) Gross error   (iv) Personal error

16. Median of the digits 2, 2, 3, 6, 5, 7, 10 is
   (i) 5   (ii) 6   (iii) 7   (iv) 10

17. The range of the digits 2, 2, 3, 6, 5, 7, 10 is
   (i) 8   (ii) 6   (iii) 10   (iv) None of these

18. The expression which states the Beer law-
   (i) $A=\varepsilon cl$ (ii) $A=\varepsilon/cl$ (iii) $A\varepsilon=cl$ (iv) None

19. For a sample interacting with radiation, the technique used is-
   (i) Conductometry   (ii) Mass spectrometry
   (iii) UV-visible spectroscopy (iv) TGA

20. Based on electrical properties of the samples, the techniques used are-
   (i) TGA, DTA   (ii) DTA, Mass Spectrometry
   (iii) Conductivity, Potentiometry (iv) Isotope analysis method

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