Registration Number:

Date & Session:

ST JOSEPH'S UNIVERSITY, BENGALURU -27
M.Sc. Chemistry – I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2023
(Examination conducted in November/ December 2023)
CH 7522: Principles of Chemical Analysis
(for current batch students only)

Time: 2 Hours **Max. Marks: 50**

This question paper contains THREE printed pages and THREE parts.

Part A

Answer any EIGHT questions. Each question carries TWO marks. (8 x 2= 16)

1. Calculate Q value for the following five data points: 2, 3, 6, 5, 10 and check if there is an outlier at the 95% confidence level (Q_{crit} = 0.710).
2. Give an example of a specific reagent and a selective reagent used for gravimetric precipitation.
3. Write the Von Weymarn's equation and explain the terms.
4. List two mechanisms of precipitation in gravimetry with their characteristics.
5. Mention any two differences between kinetic and equilibrium methods of analysis.
6. Calculate the pH of a solution prepared by adding 30.0 cm^3 of 0.10M sodium hydroxide to 25.0 cm^3 of 0.10 M acetic acid ($k_a = 1.8 \times 10^{-5}$).
7. Under what conditions the titration curve of a red-ox titration is symmetrical about the equivalence point?
8. Why does the charge on the surface of a precipitate change sign at the equivalence point in a titration? How is this change helpful in precipitation?
9. Illustrate the use of CN^- as a titrant in complexometric titration with suitable example.
10. Multidentate ligands are selected as titrants for complexometric titrations. Give reasons.

Part B

Answer any TWO questions. Each question carries TWELVE marks. (2 x 12= 24)

11. (a) As an analytical chemist, suppose you are developing a new method for blood urea nitrogen (BUN) determination. You want to determine whether the results obtained from your method is comparable to that of the standard method. From the following data, determine the (i) correlation coefficient and (ii) coefficient of determination and (iii) from the correlation coefficient value, state whether the correlation is fair, good or excellent.

Data Table:

Sample	Your method (mg/dL) x_i	Standard method (mg/dL) y_i	$x_i\, y_i$
A	10.2	10.5	107.10
B	12.7	11.9	151.13
C	8.6	8.7	74.82
D	17.5	16.9	295.75
E	11.2	10.9	122.08
F	11.5	11.1	127.65
N=6	$\Sigma x_i = 71.7$	$\Sigma y_i = 70.0$	

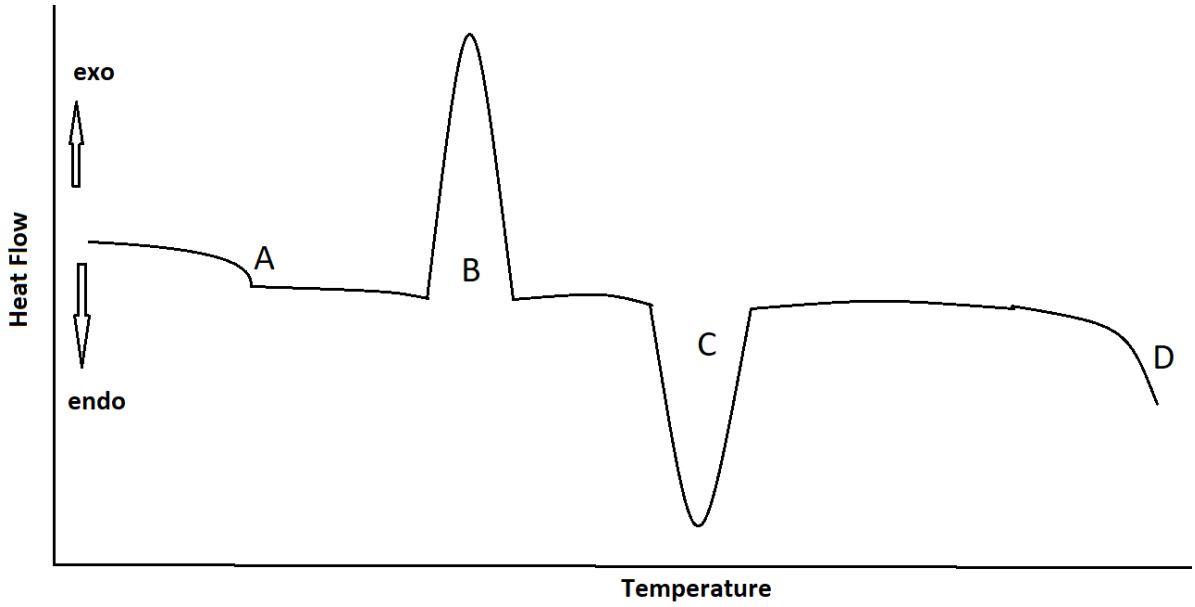
Formula to calculate the correlation coefficient is given below:

$$\frac{\Sigma(x_i\, y_i) - \mathbf{N}\,\bar{x}\,\bar{y}}{\sqrt{[\Sigma(x_i{}^2) - \mathbf{N}\,\bar{x}^2]\,[\Sigma(y_i{}^2) - \mathbf{N}\,\bar{y}^2]}}$$

(b) Explain two-point fixed-time integral method and using this method, derive an expression for the determination of initial concentration assuming pseudo first order kinetics. What are the advantages of one-point fixed-time integral method and two-point fixed-time integral method? (6+6)

12. (a) Explain ionization interferences encountered in the AAS technique.
(b) What are the criteria to choose between nephelometry and turbidimetry?
(c) What is Karl Fischer reagent? Describe how the water content in a sample is determined by Karl-Fischer titration. (3+3+6)

13. (a) Obtain expressions for various species of H_3PO_4 in terms of its dissociation constants K_1, K_2 and K_3.
(b) Calculate pAg at different stages in the titration of 10.0 cm^3 of 0.1N KCl with 5.0 and 8.0 cm^3 of 0.2N $AgNO_3$ at 25°C (K_{sp} = 1.0×10^{-10}).
(c) The following is the DSC curve of a polymer. Identify the regions marked A, B, C and D.



(4+4+4)

Part C

Answer any TWO questions. Each question carries FIVE marks. (2 x 5= 10)

14. An analytical laboratory developed a procedure A for determining glucose in serum and is compared to the established procedure B as given in the following table. Both the methods are performed on serum from the same 6 patients in order to eliminate patient-to-patient variability. Apply hypothesis testing and comment on the results from the two methods at 95% confidence level.

Patients	1	2	3	4	5	6
Procedure A (mg/L glucose)	1044	720	845	800	957	650
Established procedure B (mg/L glucose)	1028	711	820	795	935	639
Difference	16	9	25	5	22	11

Values of 't' for various levels of probability					
Degrees of freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96

15. (a) Calculate the gravimetric factor of Cr_2O_3 when it is precipitated as Ag_2CrO_4?
(b) A mixture of NaOH and Na_2CO_3 is titrated with 0.10M HCl. The phenolphthalein end point occurs at 15.0 cm^3 and the methyl orange end point occurs at 25.0 cm^3.
(i) Can $NaHCO_3$ exist in the mixture?
(ii) What type of reaction corresponds to first and second end point? (3+2)

16. A 0.3284g sample of brass (composition: Pb, Zn, Cu and Sn) was dissolved in nitric acid. The insoluble tin oxide was removed by filtration. The combined filtrate and washings were diluted to 500 cm^3. 10.0 cm^3 of this solution buffered to pH 10.0 required 37.6 cm^3 of 0.0025M EDTA solution. Cu in 25.0 cm^3 of fresh stock solution is masked with thiosulphate; Pb and Zn requires 27.7 cm^3 of EDTA solution. 100.0 cm^3 of fresh stock solution is masked with cyanide requires 10.8 cm^3 of EDTA solution. Determine the composition of brass.

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