

# CHEMICAL SCIENCES

Signature of Invigilators

PAPER-III

Roll No.       
(In figures as in Admit Card)

1. ....

Roll No. ....

2. ....

DEC-08/03

(in words)

Name of the Areas/Section (if any).....

Time Allowed : 2-1/2 hours]

[Maximum Marks : 200

## Instructions for the Candidates

1. Write your Roll Number in the space provided on the top of this page.
2. Write name of your Elective/Section if any.
3. Answer to short answer/essay type questions are to be written in the space provided below each question or after the questions in test booklet itself. No additional sheets are to be used.
4. Read instructions given inside carefully.
5. Last page is attached at the end of the test booklet for rough work.
6. If you write your name or put any special mark on any part of the test booklet which may disclose in any way your identity, you will render yourself liable to disqualification.
7. Use of calculator or any other Electronics Devices is prohibited.
8. There is no negative marking.
9. You should return the test booklet to the invigilator at the end of the examination and should not carry any paper outside the examination hall.

## પરીક્ષાર્થીઓ માટે સૂચનાઓ :

૧. આ પૃષ્ઠના ઉપલા ભાગે આપેલી જગ્યામાં તમારી ક્રમાંક સંખ્યા (રોલ નંબર) લખો.
૨. તમે જે વિકલ્પનો ઉત્તર આપો તેનો સ્પષ્ટ નિર્દેશ કરો.
૩. ટૂંકનોંધ કે નિબંધ પ્રકારના પ્રશ્નોના ઉત્તર દરેક પ્રશ્નની નીચે આપેલી જગ્યામાં જ લખો. વધારાના કોઈ કાગળનો ઉપયોગ કરશો નહીં.
૪. અંદર આપેલી સૂચનાઓ ધ્યાનથી વાંચો.
૫. આ ઉત્તર પોથીમાં અંતે આપેલું પૃષ્ઠ કાચા કામ માટે છે.
૬. આ ઉત્તર પોથીમાં કયાંય પણ તમારી ઓળખ કરાવી દે એવી રીતે તમારું નામ કે કોઈ ચોક્કસ નિશાની કરી હશે તો તમને આ પરીક્ષા માટે ગેરલાયક ગણવામાં આવશે.
૭. કેલક્યુલેટર અથવા ઈલેક્ટ્રોનિક્સ સાધનોનો ઉપયોગ કરવો નહીં.
૮. નકારાત્મક ગુણાંક પદ્ધતિ નથી.
૯. પ્રશ્નપત્ર લખાઈ રહે એટલે આ ઉત્તર પોથી તમારા નિરીક્ષકને આપી દેવી. પરીક્ષાખંડની બહાર કોઈ પણ પ્રશ્નપત્ર લઈ જવું નહીં.

## FOR OFFICE USE ONLY MARKS OBTAINED

Question Number	Marks Obtained	Question Number	Marks Obtained	Question Number	Marks Obtained
1.		18.		35.	
2.		19.		36.	
3.		20.			
4.		21.			
5.		22.			
6.		23.			
7.		24.			
8.		25.			
9.		26.			
10.		27.			
11.		28.			
12.		29.			
13.		30.			
14.		31.			
15.		32.			
16.		33.			
17.		34.			

Total Marks obtained .....

Signature of the co-ordinator .....  
(Evaluation)

SEAL

## LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5106	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5728	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	6	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

No.  $\pi = 3.14159$   
 $e = 2.71828$

log  $0.49715$   
 $0.43429$   
 $\ln x = \log_e x = (1/M) = \log_{10} x$   
 $\log x = \log_{10} x = M \log_e x$

No.  $(1/M) = 2.30259$   
 $M = 0.43429$   
 $0.36222$   
 $1.63778$

## LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

<i>P</i>	1	2	3	4	5	6	7	8	9	10
$\log e^P$	0.4343	0.8686	1.3029	1.7372	2.1715	2.6058	3.0401	3.4744	3.9087	4.3429
$\log e^{-P}$	1.5657	1.1314	2.6971	2.2628	3.8285	3.3942	4.9599	4.5256	4.0913	5.6571

## ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1088	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1226	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	2	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	2	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	2	3	3	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	2	3	3	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	2	3	3	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	2	3	3	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	2	3	3	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	2	3	3	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	2	3	3	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	2	3	3	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	2	3	3	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	2	3	3	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	2	3	3	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	2	3	3	4	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	2	3	3	4	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	2	3	3	4	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	2	3	3	4	5
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	2	2	3	3	4	5
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	2	2	3	3	4	5
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	2	2	3	3	4	5
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	2	2	3	3	4	5
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	2	2	3	3	4	5
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	2	2	3	3	4	5
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	2	2	3	3	4	5

Antilogarithm Chart continue on page No. 55

# CHEMICAL SCIENCES

## PAPER - III

**Note :** (i) Question No. 1 is compulsory (40 Marks). Answer it in 800 words (8 pages).

(ii) Attempt any ten questions out of the remaining 35 questions. (16 marks each). Answer each question in 300 words.

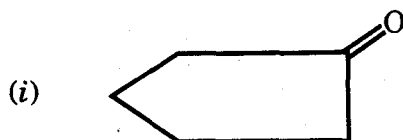
### Character Table for $C_{2V}$ point group :

$C_{2V}$	E	$C_2$	$\sigma_V (xz)$	$\sigma_V (yz)$		
$A_1$	1	1	1	1	Z	$X^2 Y^2 Z^2$
$A_2$	1	1	-1	-1	$R_Z$	XY
$B_1$	1	-1	1	-1	X, $R_y$	XZ
$B_2$	1	-1	-1	1	Y, $R_x$	YZ

1. (a) Explain the principles of emission spectroscopy based on inductively coupled plasma source. 10
- (b) A 50.0 cm<sup>3</sup> aliquot of well water is treated with an excess of KSCN and diluted to 100 cm<sup>3</sup>. Calculate the PPM of iron (III) in the sample if the diluted solution has an absorbance of 0.394 at 580 nm when measured in a 2.50 cm cell. The molar absorptivity of the complex Fe SCN<sup>2+</sup> at this wavelength is 7.00 × 10<sup>3</sup> dm<sup>3</sup> cm<sup>-1</sup> mol<sup>-1</sup>.  
 [Given : At. wt. of Fe = 55.85] 10
- (c) Match the entries in Column A with those given in Column B : 10

#### Column A

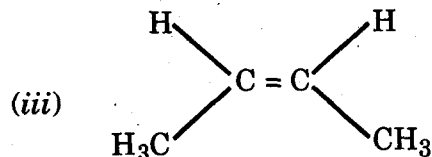
#### Column B



(1)  $\delta : 2.3$



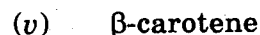
(2) 1745 cm<sup>-1</sup>



(3) J = -8 Hz



(4) 472, 478 nm



(5) m/z : 720 (m<sup>+</sup>)

(i) ..... (ii) ..... (iii) ..... (iv) ..... (v) .....

(d) (i) Explain why protons in different chemical environments show resonance at different fields in NMR. 4

(ii)  $I_A$ ,  $I_B$  and  $I_C$  are moments of inertia for rotation about the three perpendicular axes. Give the classification of molecules on this basis. Calculate the moment of inertia of carbon monoxide if the first line in the rotation spectrum appears at  $3.84235 \text{ cm}^{-1}$ .

(Given  $h = 6.626 \times 10^{-34} \text{ J.s.}$ ) 6

2. (a) Explain briefly the concept of electrical double layer in electrochemical measurements. 6

(b) Calculate the e.m.f. of the following cell at  $25^\circ\text{C}$ .

$\text{Pb}|\text{Pb}^{2+} (a = 0.0018 \text{ M}) || \text{Fe}^{2+} (a = 0.2 \text{ M}), \text{Fe}^{3+} (a = 0.15 \text{ M})|\text{Pt}$

(Given :

$$E^0 (\text{Pb}^{2+}, \text{Pb}) = - 0.126 \text{ V}$$

$$E^0 (\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.771 \text{ V}). 6$$

(c) What is a three-electrode cell ? Describe the role of each electrode in electrochemical measurements. 4

3. (a) Draw schematic diagram of a hollow cathode lamp and explain its role in atomic absorption spectroscopy. 6

(b) A  $50 \text{ cm}^3$ ,  $0.150 \text{ M}$  solution of analyte X is treated with four  $10.0 \text{ cm}^3$  portions of *n*-hexane. Calculate the concentration of X remaining in the aqueous phase after the extraction. 6

(Given : The distribution coefficient for X between *n*-hexane and water is 9.6)

(c) Give important applications of size exclusion chromatography. 4

4. (a) Draw the cyclic voltammogram for a potassium ferricyanide solution with  $\text{KNO}_3$  as supporting electrolyte at a Pt microelectrode and explain its nature. Give the criteria for reversibility. 6

(b) Explain the determination of lead in a blood sample by differential pulse anodic stripping voltammetry. 6

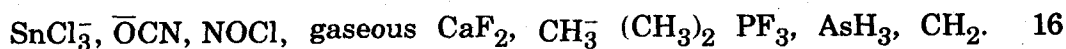
(c) What are the advantages of a dropping mercury electrode over platinum and graphite microelectrodes ? 4

5. (a) Draw molecular structures of porphirin and porphyrin. How does the conformation of hemoglobin change upon binding of the first dioxygen molecule, leading to cooperative binding of other dioxygen molecules ? 8
- (b) Why is carbon monoxide toxic to humans ? 4
- (c) Draw the structure of cis-platin. How does it work as an anti-cancer agent ? 4
6. (a) Write the formula of spinel ore. What are 'normal' and 'inverse' spinels ? Give examples. Using CFSE arguments, find out whether  $\text{Fe}[\text{Fe}_2\text{O}_4]$  has 'normal' or 'inverse' spinel structure. 8

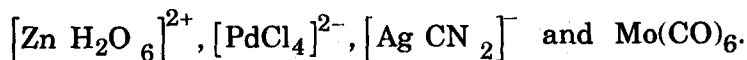
(Atomic No. of Fe = 26)

- (b) Predict Schotky and Frenkel in the following giving reasons : 8
- (i) KCl
- (ii) ZnS.
7. (a) Show that the three 'P' orbitals of oxygen atom in the water molecule ( $\text{C}_{2v}$  point group) belong to the irreducible representation  $\text{A}_1$ ,  $\text{B}_1$  and  $\text{B}_2$ . 8
- (b) The possible electronic transitions in HCHO molecule are  $n_b \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$  and  $\sigma \rightarrow \sigma^*$ . On basis of group theory, explain which of these transitions are allowed or forbidden. 8

8. Using VSEPR, work out shapes of the following species :



9. Count the number of valence electrons for the following complexes :

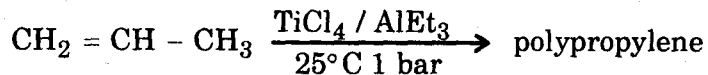


Why are the 18-electron complexes stable ? Some complexes have more than 18-electrons in their valence shells and some have less than 18. Give reasons.

(At. No. of Zn = 30, Pd = 46, Ag = 47, Mo = 42) 16

10. Calculate the magnetic moment for  $\text{Nd}^{3+}$  ion. (Nd At. No. 60). 16

11. For the following catalytic reaction, propose suitable mechanism :



What is isotactic polymer ? Why is polypropylene obtained in the above catalytic reaction isotactic ? 16

12. Draw structures of the following ligands :

Ethylenediamine, 2, 2'-bipyridine, 1, 10-phenanthroline, 8-hydroxyquinoline, oxalic acid, ethylenediamine tetra acetic acid, salicylaldehyde, dimethyl glyoxime. 16

13. (a) For the following main group elements, the lower oxidation states are more stable due to 'inert pair effect'. Giving reasons, justify the higher stability of lower oxidation states. 12

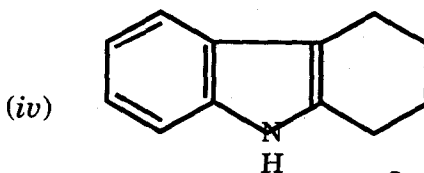
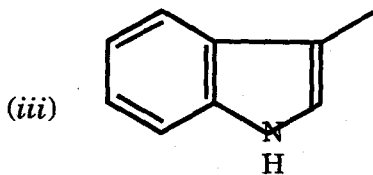
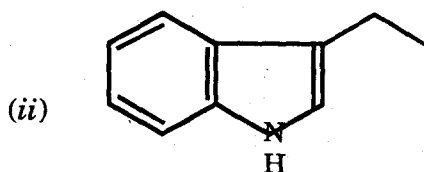
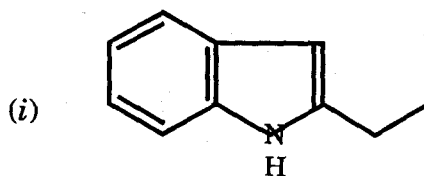
Tl, Pb, Bi, Te.

- (b) The common ores of Hg, have sulfide as the anion and not oxide. Explain. 4

14. (a) Draw possible resonance forms of tetra-sulfur-tetranitride ( $\text{S}_4\text{N}_4$ ). How is it converted to  $(\text{SN})_x$  ? Why is it a good electrical conductor ? 12

- (b) Draw structure of  $\text{IF}_7$ . 4

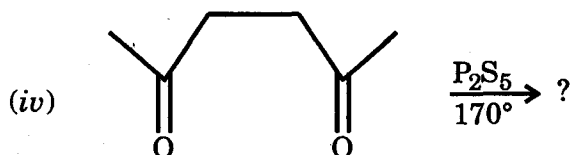
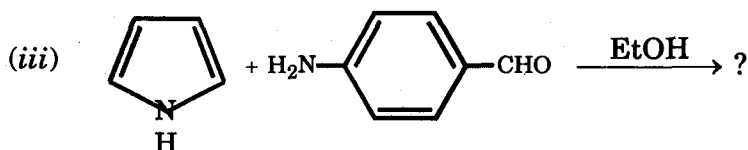
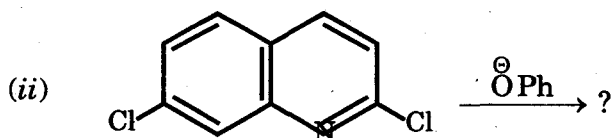
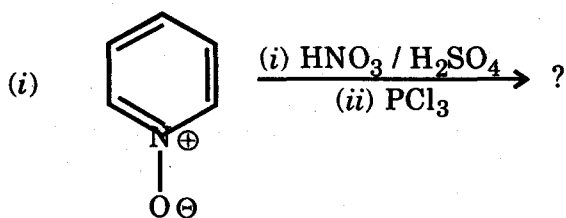
15. (A) Write the structures of the starting materials required to prepare the following compounds by Fischer indole synthesis : 8



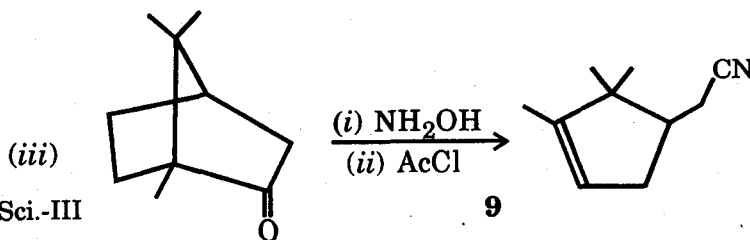
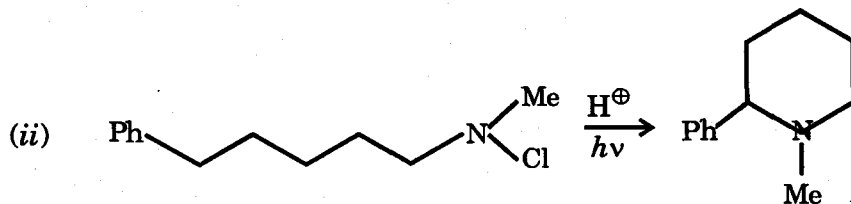
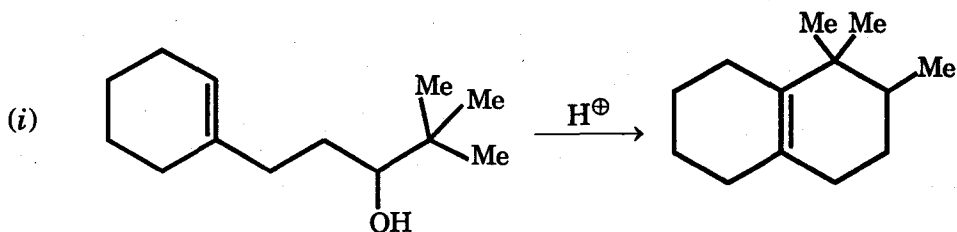


(B) Predict the products of the following reactions :

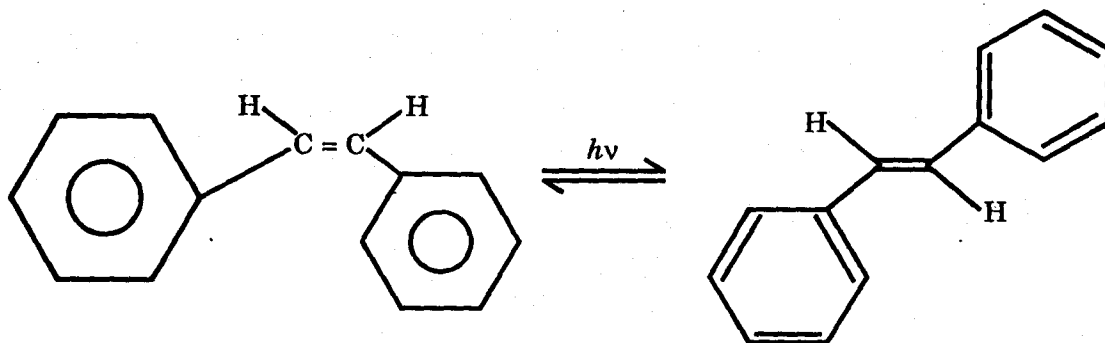
8



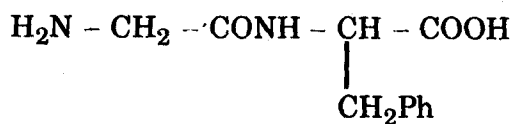
16. Suggest mechanisms for the following reactions. Name the reactions involved : 16



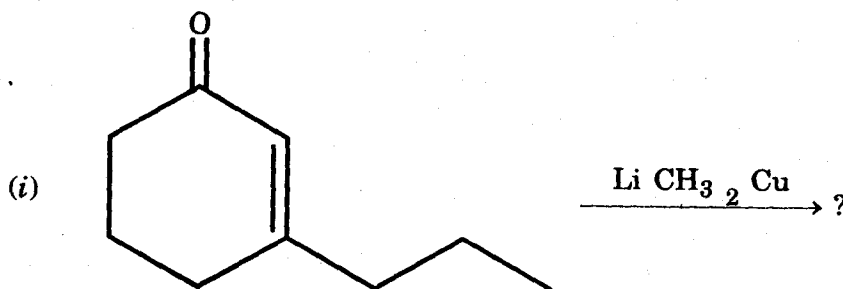
17. (A) Draw Jablonski diagram of an excited state of a molecule and describe the various deactivation pathways of the excited molecule. 8
- (B) *cis*-stilbene undergoes isomerization to *trans*-isomer upon irradiation. Provide explanation with the help of a potential energy surface diagram. 8

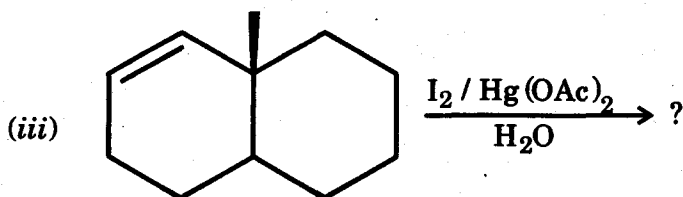
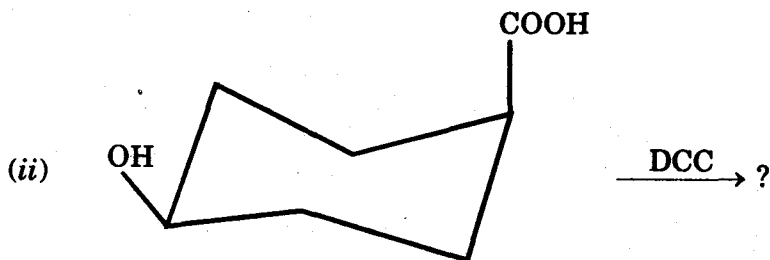


18. (A) (i) Devise synthesis of the following peptide using Merrifield solid phase method. 4

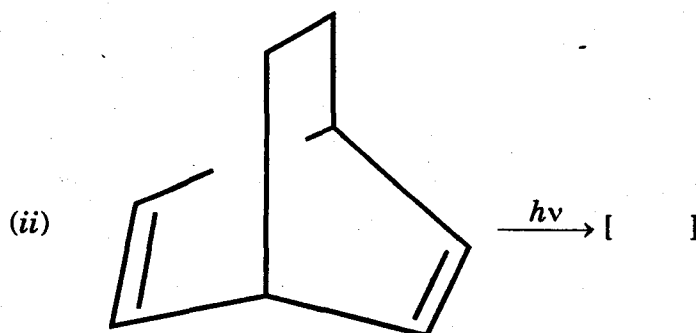
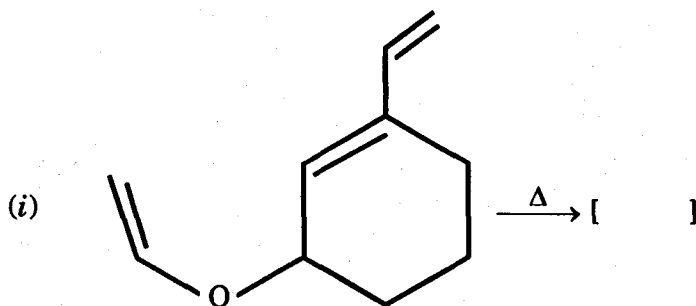


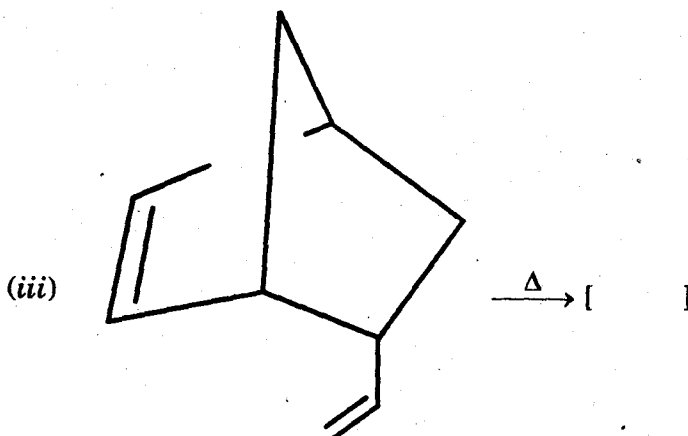
- (ii) Outline the basic differences between DNA and RNA. 4
- (B) Predict products and their stereochemistry (if any) : 8



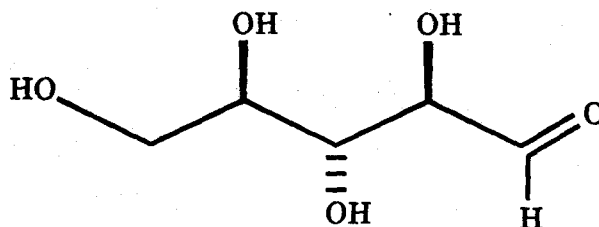


19. (A) Predict the feasibility of  $\pi^4s + \pi^2s$  cycloaddition in ground state, by using Frontier orbital approach. 8
- (B) Write structure of products in the reactions given below and suggest mechanism. 8

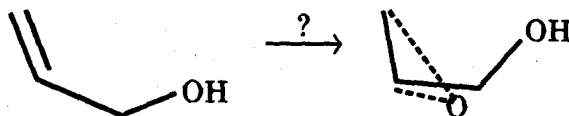




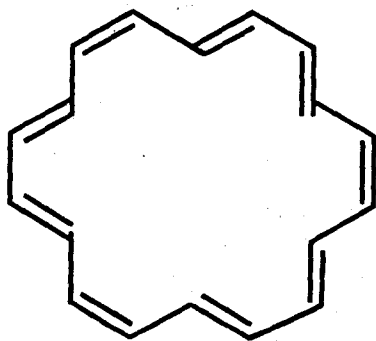
20. (A) Assign (R)-/(S)- configuration to each stereocentre in the following compound. Also indicate the priority of groups and show assignments. 8



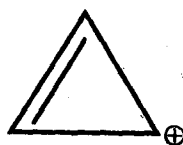
- (B) Suggest the set of reagents required for sharpless epoxidation (given below). Suggest the roles of reagents and mention which reagent gives electrophilic oxygen. 8



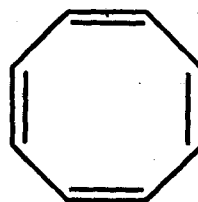
21. (A) Classify the following molecules into aromatic, antiaromatic, non-aromatic. Suggest reason for your answer. 8



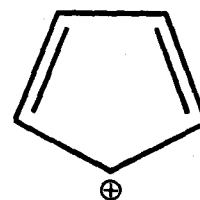
(i)



(ii)



(iii)



(B) Fullerene (C-60) is a new allotrope of carbon. Answer the following : 8

(i) How many pentagons and hexagons are present in it ?

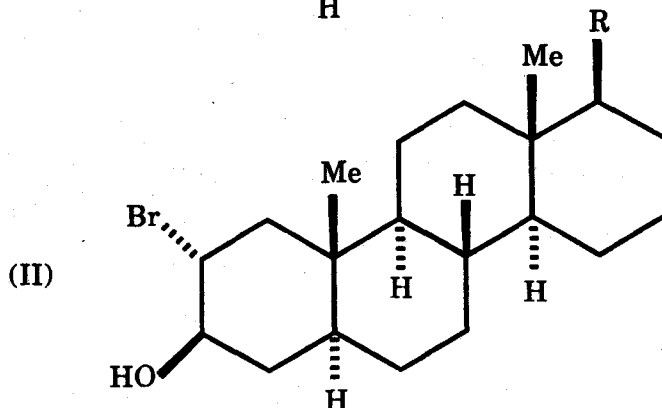
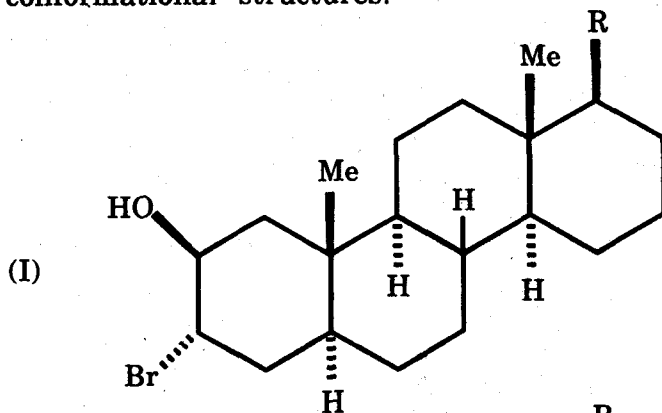
(ii) How many signals it will show in its  $^{13}\text{C}$ -NMR spectrum ?

22. (A) Write conformational structures and predict their stability and give explanation : 8

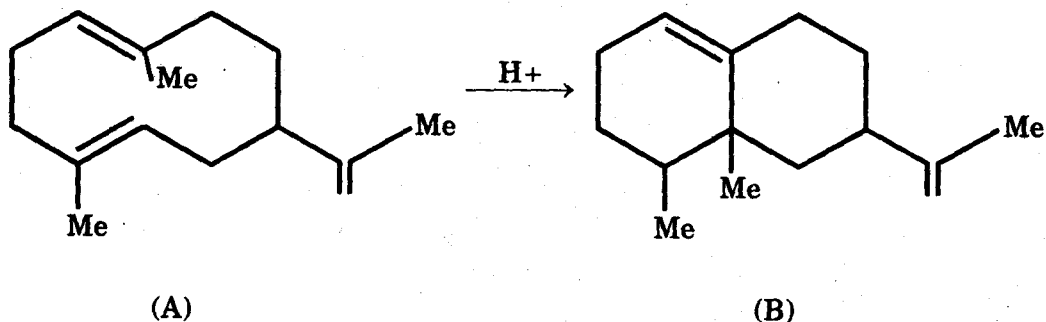
(i) *cis*- and *trans*-1, 3-dimethyl cyclohexanes

(ii) *cis*-1-*t*-Butyl-4-methyl cyclohexane.

(B) The bromohydrin I reacts with cold NaOH to give the corresponding epoxide in just 30 seconds. On the other hand the compound II gives corresponding epoxide after heating with aq. NaOH for 75 hrs. Provide explanation for the observed reactivity. Use conformational structures. 8



23. The triene (A) undergoes an acid catalysed transformation to give valencies (B). Outline mechanism of the reaction. 16



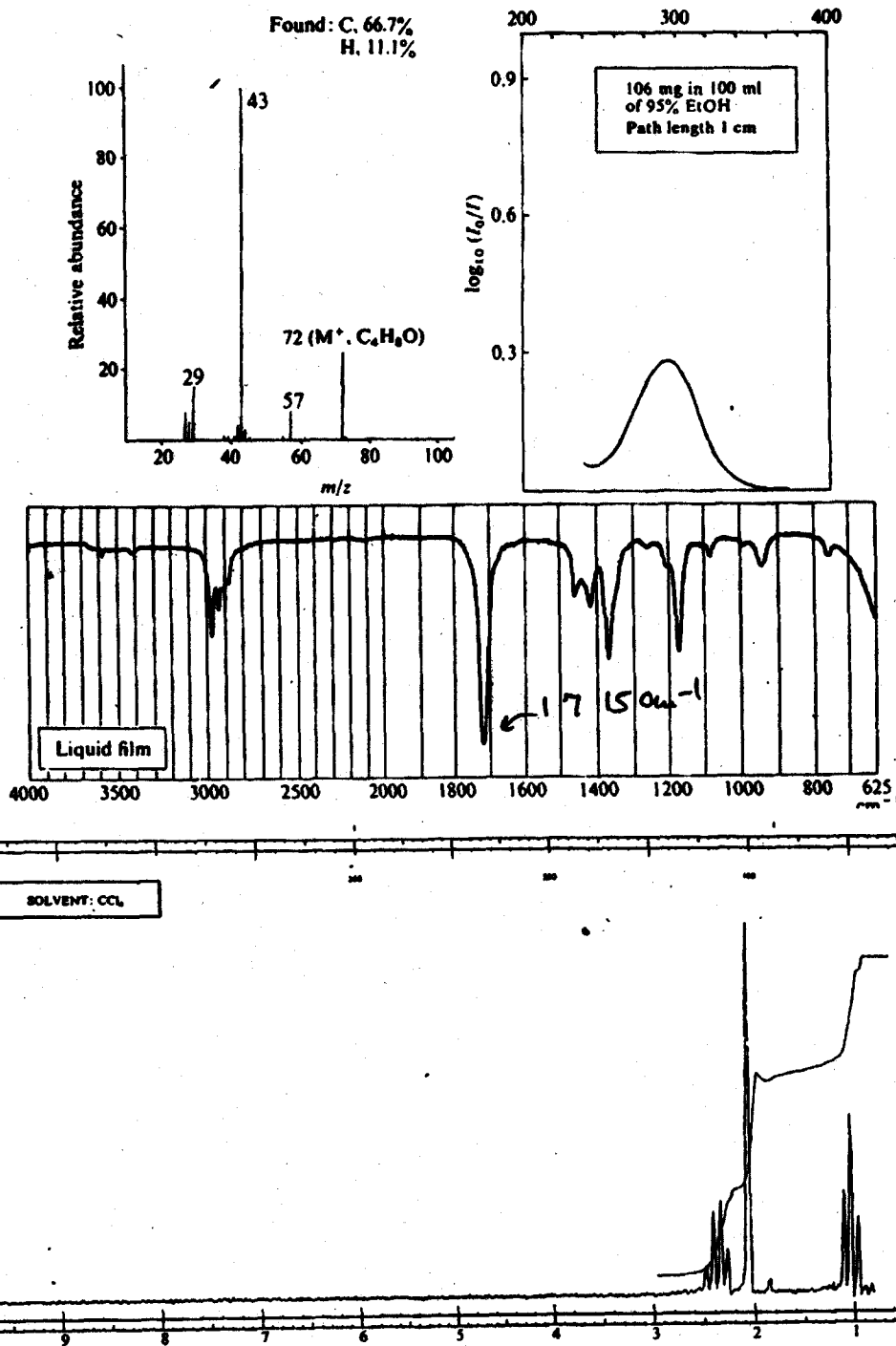
24. (A) Answer the following : 8

- (i)  $\text{KMnO}_4$  can dissolve in benzene forming purple benzene in the presence of 18-Crown-6. Draw the structure of the complex and label guest and host.
- (ii) Cyclopentadiene labelled at methylene carbon (14C) upon reaction with base followed by regeneration shows that all carbons are equally labelled. Comment.

- (B) Match the Hammett sigma ( $\sigma$ ) values with appropriate substituents. 8

Substituent	$\sigma$
(i) $\text{P-C(CH}_3)_3$	0.44
(ii) $p\text{-NH}_2$	-0.07
(iii) $m\text{-Me}$	-0.20
(iv) $p\text{-CHO}$	-0.66

25. Deduce the structure of a compound based on the following spectra (given below). 16



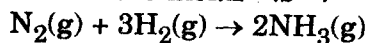
26. (a) What is the Mark-Houwink-Sakurada equation? How can the constant K and exponent 'a' be obtained experimentally and used for the determination of the molecular weight of a polymer sample? 6

- (b) What is the influence of temperature on free radical chain polymerization reaction and the molecular weight of the resulting polymer ? 5
- (c) An experiment of osmometry on polystyrene in benzene at 25°C yielded  $[\pi/C]_{C \rightarrow 0} = 0.088 \text{ atm. ml. gm}^{-1}$ . Calculate the number average molecular weight of polystyrene.  
 $[R = 82.05 \text{ atm. ml. deg}^{-1}. \text{ gm}^{-1}]$  5
27. (a) The equilibrium constant K for the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  is  $1.64 \times 10^{-4}$  at 400°C and  $0.144 \times 10^{-4}$  at 500°C. Calculate the mean heat of formation of mole of ammonia from its elements in this temperature range. 4
- (b) Explain what do you understand by the following :  
 (i) Congruent melting point;  
 (ii) Eutectic point;  
 (iii) Consolute temperature. 6
- (c) What are ideal and non-ideal solutions ? State their characteristics properties. 6
28. (a) State and explain the third law of thermodynamics. How can it be verified experimentally ? State its applications. 8
- (b) The free energy change ( $\Delta G$ ) accompanying a given process is  $-85.77 \text{ kJ mole}^{-1}$  at 25°C and  $-83.68 \text{ kJ mole}^{-1}$  at 35°C. Calculate the change in enthalpy ( $\Delta H$ ) for the process at 30°C. 8
29. (a) Compare the statistical distribution laws amongst Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics. 9
- (b) Write the statistical expression for the value of the equilibrium constant of the gaseous reaction. How one can determine its value experimentally ? 4
- (c) Define the term Partition function. State the factors affecting its value. 3
30. (a) Explain uncertainty principle. How is it relevant in explaining 'natural' line widths in spectroscopy ? To illustrate this, take the example of an excited electronic state with life time  $10^{-8}\text{s}$ . 5
- (b) Explain variation principle and estimate ground state energy of a harmonic oscillator using the trial function. 6
- (c) A certain system is described by the Hamiltonian operator : 5

$$\mathbf{H} = -\frac{d^2}{dx^2} + x^2$$

Show that  $\psi = Ax \exp(-x^2/2)$  is an eigenfunction of  $\mathbf{H}$  and determine the eigenvalue.

31. (a) Why unimolecular reactions are difficult to explain ? Discuss briefly Lindeman theory of unimolecular reactions. What are its limitations ? 9
- (b) Under certain conditions, it is found that ammonia is formed from its elements at a rate of  $0.10 \text{ mol.L}^{-1}.\text{s}^{-1}$ . 7



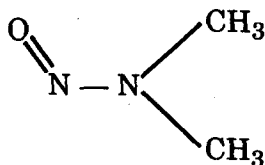
- (i) What is the rate of reaction ?



(ii) What is the value of  $\frac{d[N_2]}{dt}$  ?

(iii) What is the value of  $\frac{d[H_2]}{dt}$  ?

32. (a) Explain the effect of temperature on rates of chemical reactions and the concept of activation energy. Discuss the effect of catalyst on reaction rate in terms of activation energy. 9
- (b) For the molecule dimethylnitrosoamine 7



the rate of free rotation about N—N bond changes with temperature. Describe how NMR technique can be used to study this process.

33. (a) Define the terms surface tension and surface energy. Give the units of both. How are they related ? 6
- (b) What are catalyst promoters ? Explain their action. 5
- (c) Discuss briefly how ESCA can be used to study supported metal catalysts. 5
34. (a) Explain various types of nuclear reactions that are likely to take place as a function of energy of the projectile. Which of these can be used as an alternative source of energy and how ? 6
- (b) Derive an equation for radioactive decay constant. How this equation can be used in dating technique ? 5
- (c) Explain neutron activation analysis and give its applications. 5
35. (a) State and explain Frank-Condon principle. 3
- (b) Coupling between  $^1H$  and  $^{13}C$  appears in  $^{13}C$  NMR but not in  $^1H$  NMR why ? How this can be removed and spectra simplified ? 6
- (c) A molecule  $AB_2$  has the following IR and Raman spectra : 7

cm <sup>-1</sup>	IR	Raman
3756	Very strong	—
3652	Strong, parallel	Strong, polarized
1595	Very strong, parallel	—

The rotational fine structure of IR bands is complex and does not show simple PR or PQR characteristics. Comment on the molecular structure and assign the observed lines to specific molecular vibrations as far as possible.

36. (a) Show that for an ionic reaction :

$$\log \frac{k}{k_0} = 2 B Z_A Z_B I^{1/2},$$

where the terms have their usual meaning. 9

- (b) Explain flash photolysis and its applications. 7