Registration Number:

Date & Session:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU -27

B.Sc (CHEMISTRY) – III SEMESTER

SEMESTER EXAMINATION: OCTOBER 2022

(Examination conducted in December 2022)

CH 322 – CHEMISTRY III

Time- 2 h **Max Marks-60**

This question paper contains **THREE** printed pages, **THREE** parts and **TWENTY** questions. The periodic table is provided at the end of the question paper.

Part A

Answer any SEVEN of the following questions. **[7 × 2 = 14]**

1. Give the Lewis structure of NO_2^-. Calculate the formal charge on N in this ion.
2. Write two differences between σ and π bonds.
3. Write the autoionization reaction of a) liquid NH_3 and b) H_2O.
4. What do you mean by aprotic solvents? Give one example.
5. State zeroth law of thermodynamics.
6. Write one difference between homogeneous and heterogeneous catalysis.
7. What is the role of a catalytic promotor?
8. State Grotthus-Draper law of photochemistry.
9. Write an expression for temperature co-efficient of a reaction.

Part B

Answer any SIX of the following questions. **[6 × 6 = 36]**

10. a) Draw the Lewis structure of SF_6. Does it obey octet rule?
    b) Sketch the MO energy level diagram of N_2 molecule. **(3+3)**

11. Explain the structure of the following compounds using concept of hybridization.
    a) PCl_5 and b) CO_2 **(3+3)**

12. a) Both NH_3 and CH_4 are sp^3 hybridized but the bond angle for NH_3 is 107.5° instead of a regular tetrahedral angle. Justify.
    b) Set up the Born-Haber cycle for $CaCl_2$. From this cycle arrive at an expression for the lattice energy of $CaCl_2$. **(3+3)**

13 a) What is a levelling solvent? Explain with an example.

b) Derive an expression for the rate constant of a second order reaction when the initial concentration of the two reactants is same. **(3+3)**

14. Derive Gibbs-Helmholtz equation starting from the relation dG = VdP–SdT.

15. What is Carnot's engine? Name the working substance in it. Derive an expression for the efficiency of a Carnot's heat engine based on entropy concept.

16. a) From the values of ΔH and ΔS, predict which of the following reactions would be spontaneous at 25 °C. Show the calculation or reasoning employed to arrive at your prediction.

Reaction A: $\Delta H = 10.5\times10^3$ J; $\Delta S = 30$ JK^{-1}

Reaction B: $\Delta H = 1.8\times10^3$ J; $\Delta S = 113$ JK^{-1}

b) Write the equation for van't Hoff reaction isotherm and explain the terms involved in it. Write any one application of this equation. **(3+3)**

17. a) Sketch the Jablonski diagram and label the following: singlet states, triplet states, intersystem crossing (ISC), internal conversion (IC), fluorescence and phosphorescence.

b) Calculate the entropy change involved in the isothermal reversible expansion of 5 moles of an ideal gas from a volume of 10 L to a volume of 100 L at 300 K. [R=8.314 J K^{-1} mol^{-1}] **(3+3)**

Part C

Answer any <u>TWO</u> of the following questions. [5 × 2 = 10]

18. a) Which of these species has a higher bond length, B_2 or B_2^+? Explain.

b) The compound IF_7 has been prepared, but a similar compound FCl_7 has never been prepared. Give an explanation based on the bonding theories that you have studied. **(2+3)**

19. a) In each of the following pairs find which system has higher value of entropy?

i. CO_2 at 15 °C and 1 atm or dry ice at 1 atm

ii. One mole of $CaCO_{3(s)}$ or a mixture of $CaO_{(s)}$ and $CO_{2(g)}$ in equal quantities

b) Give reasons for the following:

i) AgI_2^- complex is more stable than AgF_2^- complex.

ii) BF_3 readily combines with F^- to form stable complex BF_4^-. **(2+3)**

20. a) The standard free energy of the formation of H_2S at 298 K is -32.94 kJ/mol. Calculate the equilibrium constant (K_p). [R= 8.314 J K^{-1} mol^{-1}]

b) Explain why N_2 has zero entropy at 0 K but CO and NO do not have zero entropy at 0 K. **(3+2)**

Periodic Table of the Elements

1 IA 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.933	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.732	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.922	34 **Se** Selenium 78.09	35 **Br** Bromine 79.904	36 **Kr** Krypton 84.80
37 **Rb** Rubidium 84.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.327	57-71	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.967	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]	113 **Uut** Ununtrium unknown	114 **Fl** Flerovium [289]	115 **Uup** Ununpentium unknown	116 **Lv** Livermorium [298]	117 **Uus** Ununseptium unknown	118 **Uuo** Ununoctium unknown

Lanthanide Series	57 **La** Lanthanum 138.906	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.24	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.966	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
Actinide Series	89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]