Syllabus: CHEM 111

Periodic Table

1. Write a short note on the Modern Periodic Table.
2. How can you determine the position on an element in the periodic table
3. Write a short note on the following:
    I. Metals
    II. Metalloids
    III. Non-Metals
    IV. Transition Metals
    V. Why are d-block elements colorful?
4. Identify the metals, metalloids, transition metals, noble gases and non-metals from the given elements with appropriate explanation. Also mention the group and period of each.

Na, Al, F, Si, Ge, Ar, Kr, Ag, Au, Zn, K, Sc, Cr, Fr, P, S, Mn

Chemical Bonding

1. What is meant by hybridization? Write the hybridisation involved in (i) Beryllium dichloride and (ii) Boron trifluoride.
2. Describe sp3, sp2 and sp hybridization of carbon in organic molecules given below:

CH_4, C_2H_4, C_2H_2, C_6H_6

3. CH_4, NH_3 and H_2O have tetrahedral geometry yet their bond angles are different. Why?
4. Explain the structure of the following molecules on the basis of hybridization:

SF_4, SF_6, PCl_3, PCl_5

5. Draw the molecular orbital picture of NO and CO. Comment on their bond order and magnetism.
6. Draw the molecular orbital diagram of O_2 and O_2^{2-}. Comment on their bond order and magnetism.

Thermochemistry

1. Differentiate between endothermic and exothermic process.
2. State and explain heat of formation, heat of combustion and heat of neutralisation with examples.
3. State and explain Hess's law of constant heat summation.
4. Calculate ΔH^{o} for the reaction CO_2 (g) + H_2(g) → CO(g) + H_2O(g) given that ΔH of for CO_2(g), CO(g) and H_2O(g) are – 393.5, – 111.31 and – 241.80 kJ mol^{-1} respectively.
5. The standard heats of formation of C_2H_5OH (l), CO_2 (g) and H_2O (l) are – 277.0, –393.5 and –285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction: $C2H_5OH$ (l) + $3O_2$(l) → $2CO_2$(g) + $3H_2O$(l)

Chemical kinetics

1. Differentiate between molecularity and order.
2. Define order of a reaction, molecularity of a reaction and half-life period. Show that for first order reactions the half-life period is independent of the initial concentration.
3. Deduce the rate expression for second order reaction where both the concentration terms are same. What is half-life period of the second order reaction?
4. Describe the graphical method for the determination of order of reaction.
5. Derive the integrated Arrhenius equation of activation energy. How is the energy of activation determined from the plot?
6. A solution of H_2O_2 when titrated against $KMnO_4$ solution at different time intervals gave the following results :

t (minutes)	0	10	20
Vol $KMnO_4$ used for 10 ml H_2SO_4	23.8 ml	14.7 ml	9.1 ml

Show that the decomposition of H_2O_2 is a first order reaction.

7. **SOLVED PROBLEM.** The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first order reaction.

t (secs)	0	4500	7140	∞
ml alkali used	24.36	29.32	31.72	47.15

8.

SOLVED PROBLEM. Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

t (mts)	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

9. Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is $0.450 s^{-1}$. What is the half-life of A at 25°C?
10. The rate law for the decomposition of N_2O_5 (l) is: rate = k $[N_2O_5]$ where k = 6.22×10^{-4} sec^{-1}. Calculate half-life of N_2O_5 (l) and the number of seconds it will take for an initial concentration of N_2O_5 (l) of 0.100 M to drop to 0.0100 M.
11. For a certain first order reaction $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75%?
12. A first order reaction is one-fifth completed in 40 minutes. Calculate the time required for its 100% completion.
13. 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.
14. The values of the rate constant (k) for the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ were determined at several temperatures. A plot of 1n k versus 1/T gave a straight line of which the slope was found to be -1.2×10^4 K. What is the activation energy of the reaction?
15.

SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation

$$CH_4(g) + 2S_2(g) \longrightarrow CS_2(g) + 2H_2S(g)$$

At 550°C the rate constant for this reaction is 1.1 $l\ mol^{-1}$ sec and at 625°C the rate constant is 6.4 1 mol^{-1} sec. Calculate E_a for this reaction.

Phase diagram

1. Discuss main features of the phase diagram of water system.
2. Discuss the salient features of phase diagram of carbon dioxide system.
3. Find out the number of degrees of freedom in the following systems:
   i. $Sulphur(l) \leftrightarrow Sulphur(vap)$
   ii. $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$
   iii. $NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$
   iv. $H_2O(s) \leftrightarrow H_2O(l) \leftrightarrow H_2O(g)$
   v. $N_2(g) + O_2(g) \leftrightarrow 2NO(g)$
   vi. $Na_2SO_4 .10H_2O \leftrightarrow Na_2SO_4 + 10H_2O(g)$

pH and Buffer

1. What are buffer solutions? Derive Henderson's equation to calculate the pH of an acidic buffer and basic buffer solution.
2. Explain with an example why pH of a buffer solution does not change significantly on small addition of acids or bases.
3. Find the pH of a buffer solution containing 0.20 mole per litre CH_3COONa and 0.15 mole per litre CH_3COOH. Ka for acetic acid is 1.8×10^{-5}.
4. Estimate the pH at 25°C containing 0.10 M sodium acetate and 0.03 M acetic acid pKa for $CH_3COOH = 4.57$.
5. Calculate the pH of a buffer solution that is 0.250 M in formic acid, HCOOH, and 0.100 M in sodium formate, HCOONa. Ka for formic acid is 1.8×10^{-4}.
6. A buffer solution contains 0.015 mole of ammonium hydroxide and 0.025 mole of ammonium chloride. Calculate the pH value of the solution. Dissociation constant of NH_4OH at the room temperature is 1.80×10^{-5}.
7. A buffer solution contains 0.25 M NH_3 and 0.40 M NH_4Cl. Calculate the pH of the solution. K_b for ammonia = 1.8×10^{-5}.

Electrical properties of Solution

1. Define conductance, specific conductance, equivalent conductance and molar conductance.
2. Explain the factors affecting the conductance of an electrolyte.
3. On progressive dilution, specific conductance of an electrolyte decreases but molar conductance increases" discuss.
4. 0.5 Normal solution of a salt placed between two platinum electrodes, 20 cm apart and of area of cross-section 4.0 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.
5. The resistance of a N/10 solution of a salt is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution. Cell constant = 1.15 cm^{-1}.
6. The resistance of a 1N solution of salt is 50 ohms. Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1cm apart and each having an area of $4.2cm^2$.
7. Which of the following have maximum molar conductivity.
   (i) 0.08M solution and its specific conductivity is 2 × 10–2 $ohms^{-1}$ cm^{-1}.
   (ii) 0.1M solution and its resistivity is 50 ohms cm.

Selective Organic Reactions: Oxidation-reduction, Substitution, Addition, Polymerization, Alkylation reactions.