

NGOKO CHEMISTRY SERIES

CHEMISTRY HOME PACKAGE

ATOM

1. Uranium has atomic number 92 and atomic weight 238.029. Give the number of electrons, protons and neutrons in its atom.
2. The wavelength of a violet light is 400 nm. Calculate its frequency and wave number.
3. The frequency of strong yellow line in the spectrum of sodium is $5.09 \times 10^{14} \text{ sec}^{-1}$. Calculate the wavelength of the light in nanometers.
4. Calculate the magnitude of the energy of the photon (or quantum) associated with light of wavelength 6057.8 Å. ($\text{Å} = 10^{-8} \text{ cm}$)
5. What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is $1.3 \times 10^{15} \text{ sec}^{-1}$.
6. Calculate the kinetic energy of an electron emitted from a surface of potassium metal (work function = $3.62 \times 10^{-12} \text{ erg}$) by light of wavelength $5.5 \times 10^{-8} \text{ cm}$.
7. Find the wavelength in Å of the line in Balmer series that is associated with drop of the electron from the fourth orbit. The value of Rydberg constant is $109,676 \text{ cm}^{-1}$.
8. (a) State the postulates of Bohr's theory of the hydrogen atom. Derive an expression for the nth orbit of a hydrogen atom. Derive an expression for the radius of any orbit in the atom.
(b) Calculate the energy of transition involving $n_1 = 6$ to $n_2 = 3$ in a hydrogen atom, given that Rydberg constant $R = 109737.32 \text{ cm}^{-1}$ and $h = 6.63 \times 10^{-34} \text{ J sec}$. **Answer. (b) $1.818 \times 10^{-19} \text{ J}$**
9. Give an account of Bohr's theory of atomic structure and show how it explains the occurrence of spectral lines in the atomic spectra of hydrogen.
10. The electron energy in hydrogen atom is given by $E = -21.7 \times 10^{-12}/n^2 \text{ ergs}$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition? **Answer. $-5.42 \times 10^{-12} \text{ erg}$; $3.67 \times 10^{-5} \text{ cm}$**
11. In a hydrogen atom, an electron jumps from 3rd orbit to first orbit. Find out the frequency and wavelength of the spectral line. **Answer. 1025.6 Å**
12. The energy of the electron in the second and third orbits of the hydrogen atom is $-5.42 \times 10^{-12} \text{ erg}$ and $-2.41 \times 10^{-12} \text{ erg}$ respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit. **Answer. 6600 Å**
13. Calculate the wavelength in Å of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionisation potential in the ground state of hydrogen atom is $2.17 \times 10^{-11} \text{ erg per atom}$. **Answer. 1220 Å**

14. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ transition? **Answer. $n = 2$ to $n = 1$**
15. (a) State postulates of Bohr's theory of an atom and derive an expression for radius of Bohr orbit of hydrogen atom.
(b) Give any four limitations of Bohr's theory of an atom.
16. Describe Rutherford's model of the atom. How was it improved by Bohr?
17. Atomic hydrogen is excited to the 4th energy level from the ground state. Determine (a) the number of lines emitted and (b) the shortest wavelength present in the emission spectrum. ($R_H = 109677 \text{ cm}^{-1}$) **Answer. (a) 3; (b) 972.55 \AA**
18. Radius of the first Bohr orbit of H-atom is 0.529 \AA . Find the radii of the first and second Bohr orbit of Li^{2+} ion. **Answer. (a) 0.1763 \AA ; (b) 0.7053 \AA**
19. If the energy difference between the ground state of an atom and its excited state is $4.4 \times 10^{-19} \text{ J}$, what is the wavelength of the photon required to produce this transition? **Answer. $4.517 \times 10^{-7} \text{ m}$**
20. 26. Calculate the wavelength and energy of radiations emitted for the electronic transition from infinity (∞) to stationary state of the hydrogen atom. ($R = 1.09678 \times 10^7 \text{ m}^{-1}$; $h = 6.625 \times 10^{-34} \text{ Joule sec}$ and $c = 2.9979 \times 10^8 \text{ m sec}^{-1}$) **Answer. $9.11 \times 10^{-6} \text{ m}$; $217.9 \times 10^{-23} \text{ kJ}$**
21. 27. The energy transition in hydrogen atom occurs from $n = 3$ to $n = 2$ energy level. ($R = 1.097 \times 10^7 \text{ m}^{-1}$).
(a) Calculate the wavelength of the emitted electron.
(b) Will this electron be visible?
(c) Which spectrum series does this photon belong to?
22. 28. Calculate the energy emitted when electrons of 1.0 g of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum ($R = 1.1 \times 10^7 \text{ m}^{-1}$; $c = 3 \times 10^8 \text{ m sec}^{-1}$; $h = 6.62 \times 10^{-34} \text{ J sec}$) **Answer. 182.5 kJ**
23. In hydrogen atom the energy of the electron in first Bohr's orbit is $-1312 \times 10^5 \text{ J mol}^{-1}$. What is the energy required for the excitation of second Bohr's orbit? **Answer. $9.84 \times 10^5 \text{ J mol}^{-1}$**
24. Calculate the wavelength in \AA of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionisation potential in the ground state of hydrogen atom is $2.17 \times 10^{-11} \text{ erg per atom}$. **Answer. 1220 \AA**
25. A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the n th to 2nd Bohr orbit. What is the value of n ? **Answer. $n = 5$**
26. The energy transition in hydrogen atom occurs from $n = 3$ to $n = 2$ energy level. ($R = 1.097 \times 10^7 \text{ m}^{-1}$).
(i) Calculate the wavelength of the emitted electron
(ii) Will this electron be visible?
(iii) Which spectrum series does this photon belong to? **Answer. 6564 \AA ; Yes; Balmer series**

27. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit. **Answer. 6600 Å**
28. Calculate the wavelength of the first line in Balmer series of hydrogen spectrum. ($R = 109677 \text{ cm}^{-1}$) **Answer. 1215 Å**
29. (a) How does Bohr's theory explain the spectrum of hydrogen atom?
 (b) Calculate the wavelength associated with an electron moving with a velocity of $1 \times 10^8 \text{ cm sec}^{-1}$. Mass of an electron = $9.1 \times 10^{-28} \text{ g}$ **Answer. (b) $7.28 \times 10^{-8} \text{ cm}$**
30. A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the n th to 2nd Bohr orbit. What is the value of n ? **Answer. $n = 5$**

CHEMICAL BONDING

1. (a) Why the bond angle in H_2S is less than H_2O ?
 (b) Explain the structure and hybridization of SO_4^{2-} ion.
 (c) Explain the structure and various bond angles in IF_7 .
 (d) Why is the bond angle of OF_2 smaller than that of Cl_2O ?
2. (a) What are the characteristics of hybrid orbitals?
 (b) What is tetrahedral hybridization? Explain the formation of C–H bonds in CH_4 .
 (c) What are sigma (σ) and pi (π) bonds? Distinguish between them.
3. . Explain the state of hybridization of oxygen atom in water and indicate its shape.
4. What is pi bond? Explain the formation of pi bond in ethylene and acetylene.
5. What is meant by hybridization?
6. Explain sp , sp^2 and sp^3 hybridization with the help of simple organic molecules. Indicate the shape of the molecule in each case
7. . (a) What is a molecular orbital? In what ways is a molecular orbital different from a valence bond orbital?
 (b) Sketch and describe the molecular orbital resulting from the following overlaps of atomic orbitals:
 - (i) Two s-orbitals
 - (ii) Head-on overlap of two p-orbitals
8. (a) What is hybridization? Write down the rules for hybridization of orbitals.
 (b) CH_4 , NH_3 and H_2O have tetrahedral geometry yet their bond angles are different. Why?
9. What is meant by hybridization? Write the hybridisation involved in
 - (i) Beryllium dichloride and
 - (ii) Boron trifluoride.
10. The molecules of CH_4 (methane), NH_3 (Ammonia) and H_2O (water) all involve sp^3 hybridization of the central atom but the bond angles in these molecules are $109^\circ 28'$, $107^\circ 18'$ and $104^\circ 30'$ respectively. Explain.

11. What is meant by an ionic bond? What are the conditions necessary for the formation of an ionic bond?
12. Describe the basic ideas of the VSEPR theory. Explain the application of the theory for predicting the shapes of the molecules, BCl_3 , NH_3 , H_2O and SF_6 .
13. (a) What are electrovalent compounds? Discuss various factors which affect the formation of these compounds.
(b) What do you understand by hydrogen bonds? Classify them with examples. Explain why water has abnormally high boiling point.
14. Why bond angles of H_2O and NH_3 are 104.5° and 107° respectively although central atoms are sp^3 hybridized.
15. (a) What do you understand by 'Stable configuration'? What are the ways by which an atom can attain stable configuration?
(b) Write the electronic configuration of any two of the following compounds :
(i) Phosphorus pentachloride (ii) Sulphuric acid (iii) Lithium fluoride
16. What type of bonds do you expect in the following cases? Give reasons :
(i) between a very small cation and a large anion.
(ii) between atoms having a very large difference in electronegativities,
(iii) between atoms of the same element.
17. What is electronegativity? How is the concept of electronegativity used to predict the bond types between hetero atoms?
18. Indicate the type of bonding that exists in the following solids :
(i) Ice (ii) Naphthalene (iii) Diamond (iv) Potassium chloride
19. What is a co-ordinate covalent bond? How does it differ from a normal covalent bond? Discuss the shape of the following molecules on the basis of VSEPR theory : NH_3 , CH_4 , PCl_3
20. Explain the formation of NH_3 molecule if no hybridization of s and p-orbitals of nitrogen is assumed.
21. Two elements X and Y occur in the same period and their atoms have two and seven valence electrons respectively. Write down the electronic structure of the most probable compound between X and Y. Will the bond between X and Y be predominantly ionic or covalent?
22. Classify the bonds in the following as ionic, polar covalent or covalent
(a) HCl (b) NaCl and (c) NCl_3 .

Answer. XY_2 ; Ionic

Answer. HCl - Polar covalent, NaCl - Ionic and NCl_3 – Covalent

GASES

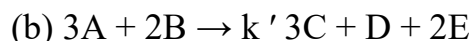
- 25.8 litre of a gas has a pressure of 690 torr and a temperature of 17°C. What will be the volume if the pressure is changed to 1.85 atm and the temperature to 345 K. = **15.1L**
- What pressure is exerted by a mixture of 2.00 g of H₂ and 8.00 g of N₂ at 273 K in a 10 litre vessel ? = **2.84atm**
- A sample of oxygen is collected by the downward displacement of water from an inverted bottle. The water level inside the bottle is equalised with that in the trough. Barometric pressure is found to be 757 mm Hg, and the temperature of water is 23.0°C. What is the partial pressure of O₂ ? Vapour pressure of H₂O at 23°C = 19.8 mm Hg. = **737.2mmhg**
- If a gas diffuses at a rate of one-half as fast as O₂, find the molecular mass of the gas. **Mr=128g/mol**
- 50 ml of gas A effuse through a pin-hole in 146 seconds. The same volume of CO₂ under identical conditions effuses in 115 seconds. Calculate the molecular mass of A. **Mr =71gmol⁻¹**
- Calculate the root mean square velocity of CO₂ molecule at 1000°C = **849.85 m sec⁻¹**
- Oxygen at 1 atmosphere pressure and 0°C has a density of 1.4290 grams per litre. Find the RMS velocity of oxygen molecules. = **46138 cm sec**
- Calculate the pressure exerted by 1.00 mole of methane (CH₄) in a 250 mL container at 300 K using van der Waals equation. What pressure will be predicted by ideal gas equation ? a = 2.253 L² atm mol⁻², b = 0.0428 L mol⁻¹; R = 0.0821 L atm mol⁻¹ K. = **98.5 atm**
- One mole of water vapour is confined to a 20 litre flask at 27°C. Calculate its pressure using
 - van der Waal's equation
 - Ideal gas equation
 Given that a = 5.464 litre² atm mol⁻¹ b = 0.0305 litre mol⁻¹
 R = 0.0821 litre atm. deg⁻¹ mol⁻¹
- Two moles of NH₃ are enclosed in a five litre flask at 27°C. Calculate the pressure exerted by the gas assuming that
 - the gas behaves like an ideal gas.
 - the gas behaves like a real gas a=4.14 and b=0.037
- What are the limitations of the equation PV = RT? What improvements have been suggested by van der Waal?
 - How van der Waal's equation can be applied for the calculation of Boyle's temperature? Also define Boyle's temperature.
 - Show that van der Waal's equation reduces to ideal gas equation at Boyle's temperature.
- Explain the deviation of real gases from ideal gas behaviour and derive the van der Waal's equation for one mole of a gas $\left(P + \frac{a}{V^2}\right)(V - b) = RT$
- Starting from kinetic gas equation derive
 - Avogadro's law;
 - Graham's law of diffusion

SOLUTIONS

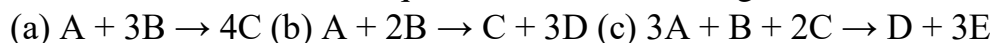
1. At a pressure of 760 mm, a mixture of nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) and water boils at 99°C . The vapour pressure of water at this temperature is 733 mm. Find the proportion of water and nitrobenzene in the distillate obtained by steam distillation of impure $\text{C}_6\text{H}_5\text{NO}_2$
2. A mixture of water and bromobenzene ($\text{C}_6\text{H}_5\text{Br}$) distills at 95°C , and the distillate contains 1.6 times as much $\text{C}_6\text{H}_5\text{Br}$ as water by mass. At 95°C the vapour pressure of water and $\text{C}_6\text{H}_5\text{Br}$ are 640 mm Hg and 120 mm Hg respectively. Calculate the molecular weight of bromobenzene
3. Nitrobenzene is completely immiscible with water. A mixture of the two liquids boils at 99°C and 753 torr pressure. The vapour pressure of water is 733 torr at this temperature. Find out the weight composition of liquid mixture.
4. A solid X is added to a mixture of benzene and water. After shaking well and allowing to stand, 10 ml of the benzene layer was found to contain 0.13 g of X and 100 ml of water layer contained 0.22 g of X. Calculate the value of distribution coefficient. =5.9
5. An aqueous solution of succinic acid at 15°C , containing 0.07 g in 10 ml is in equilibrium with an ethereal solution which has 0.013 g in 10 ml. The acid has its normal molecular weight in both the solvents. What is the concentration of the ethereal solution which is in equilibrium with an aqueous solution containing 0.024 g in 10 ml?
6. At 25°C an aqueous solution of iodine containing $0.0516\text{ g litre}^{-1}$ is in equilibrium with a carbon tetrachloride (CCl_4) solution containing $4.412\text{ g litre}^{-1}$. The solubility of iodine in water at 25°C is 0.34 g litre^{-1} . Find the solubility of iodine in carbon tetrachloride.
7. The distribution coefficient of X for benzene and water is 10. Find the amount of X extracted if 1 g of it dissolved in 100 ml of water is equilibrated in a separatory funnel with 100 ml of benzene.
8. An aqueous solution contains 10g of solute per litre. When 1 litre of the solution is treated with 100 ml of ether, 6g of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by a further 100 ml ether? Assume that the molecular state of the solute is the same in ether and water.
9. The distribution coefficient of isobutyric acid between ether and water is 3 at 25°C . What will be the amount of isobutyric acid removed if 4 g of isobutyric acid in 100 ml of water is extracted with 100 ml of ethoxyethane (ether) at 25°C . What would the effect have been if two successive 50 ml portions of ether had been used to extract the aqueous layer?
10. A solution of 6 g of substance X in 50 ml of aqueous solution is in equilibrium, at room temperature, with a solution of X in diethyl ether (ethoxyethane) containing 108 g of X in 100 ml. Calculate the mass of X extracted by shaking 100 ml of an aqueous solution containing 10 g of X with (a) 100 ml of ether; (b) 50 ml of ether twice at room temperature.

CHEMICAL KINETICS

1. Write the differential rate equations of the following reactions:
(a) $\text{A} + 2\text{B} \rightarrow \text{k P}$



2. Write the differential rate equations of the following reactions:



3. Express the rate constant k in unit of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, if

(i) $k = 2.50 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$

(ii) $k = 2 \times 10^{-6} \text{ s}^{-1} \text{ atm}^{-1}$

4. For a certain reaction, the value of rate constant is $5.0 \times 10^{-3} \text{ dm}^3 \text{mol}^{-1} \text{sec}^{-1}$. Find the value of rate constant in

(i) $\text{dm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

(ii) $\text{cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ and

(iii) $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

5. A zero order reaction is 50% complete in 20 min. How much time will it take to complete 90%?

6. A reaction is 50% complete in 20 min. How much time will be taken to complete 75% reaction?

7. The specific rotation of sucrose in presence of hydrochloric acid at 35°C was measured and is given as follows:

Time (min)	0	20	40	80	180	500	∞
Rotation ($^\circ\text{C}$)	32.4	28.8	25.5	19.6	10.3	6.1	-14.1

Calculate the rate constant at various time intervals and show that the reaction is first order.

8. A first order reaction is 25% complete in 50 min. What would be concentration at the end of another 50 min if the initial concentration of the reactant is $5.0 \times 10^3 \text{ mol dm}^{-3}$?

9. The kinetics of a reaction was followed by measuring the absorbance due to a reactant at its λ_{max} at 25°C . The $\log(\text{absorbance})$ versus time (min) plot was a straight line with a negative slope (0.30×10^{-2}) and a positive intercept. Find the half-life period of reaction.

10. In a first order reaction the $\log(\text{concentration of reactant})$ versus time plot was a straight line with a negative slope $0.50 \times 10^4 \text{ sec}^{-1}$. Find the rate constant and half-life period of reaction

11. A reactant reacts 30% in 30 min. If the reaction follows a second order kinetics, find rate constant and remaining concentration of reactant after 60 min.

12. In a reaction when initial concentration doubles, the half-life is reduced to half. What is the order of reaction?

13. A second-order reaction in which both the reactants were at same initial concentration was 50% completed in 500 sec. How long will it take to complete 75% of the reaction? Determine the rate constant also.

14. A first-order reaction has the rate constant $= 1.0 \times 10^{-4} \text{ sec}^{-1}$ at 298 K. Calculate the half-life period of the reaction

15. The values of rate constants for reaction $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ were observed as $3.0 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $2.5 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 357°C and 447°C , respectively. Calculate the E for forward and backward reaction of $\Delta H = 15.5 \text{ kJ mol}^{-1}$.

16. A first-order reaction at 25°C and 45°C has rate constants equal to 2.5×10^{-4} and $17.0 \times 10^{-4} \text{ sec}^{-1}$, respectively. Calculate Arrhenius factor and E_{act} for the reaction.

17. The values of the rate constant (k) for the reaction $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ were determined at several temperatures. A plot of $\ln k$ versus $1/T$ gave a straight line of which the slope was found to be $-1.2 \times 10^4 \text{ K}$. What is the activation energy of the reaction ?

CHEMICAL EQUILIBRIUM

1. Define or explain the following terms :
 - (a) Chemical equilibrium
 - (b) Law of mass action
 - (c) Equilibrium constant
 - (d) Heterogeneous equilibria
2. One mole of PCl_5 is heated in a closed two-litre vessel. At equilibrium 40% of the PCl_5 is dissociated. Calculate the equilibrium constant of the reaction. **Answer. 0.267**
3. (a) Why chemical equilibrium is called a dynamic equilibrium?
 (b) In what direction the following equilibrium will be shifted if some chlorine gas is introduced into the system at equilibrium? $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$
 (c) Calculate the ratio of K_p to K_c at 27°C for the equilibrium reaction: $\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g})$ **Answer. (c) 24.63**
4. For the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ the equilibrium constant at 1000 K is 0.53.
 - (a) If a mixture at equilibrium in a 1 dm³ vessel contains 0.25 mole of CO and 0.6 mole of H_2 , how many moles of H_2O are there in the vessel?
 - (b) 5 moles of inert gas are added to the equilibrium mixture containing 1 mole of H_2 and 1 mole of CO_2 in 1 dm³ vessel. Predict equilibrium concentration of CO_2 and H_2O .
Answer. (a) 0.636 mole; (b) 0.4 mole; 0.4 mole
5. (a) What is standard free energy change? Derive a relationship between standard free energy change and equilibrium constant of a reaction at a given temperature.
 (b) The equilibrium constant K_p for the reaction : $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 1.64×10^{-4} at 673 K and 0.144×10^{-4} at 773 K. Calculate the mean heat of formation of ammonia from its elements in this temperature range. **Answer. (b) -52.6174 kJ**
6. Write a short note on “Le Chatelier’s Principle”
7. (a) Define equilibrium constant and show that it can have two different values depending on how you express concentration. Derive relationship between these two values.
 (b) Equilibrium constant of the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 64 at a certain temperature. If 12 g of hydrogen and 762 g of iodine be kept in a closed vessel at this temperature to attain equilibrium what weight of HI will be present in the vessel? **Answer. 847.8 g**
8. Calculate the equilibrium constant of the reaction $\text{A} + \text{B} \rightleftharpoons 2\text{C}$ from the data given below :
 The reaction was started with 2.0 moles litre⁻¹ of A and 2.0 moles litre⁻¹ of B and the equilibrium concentration of C was found to be 0.32 mole litre⁻¹. **Answer. 0.030244.**
9. (a) Derive the relation between K_p and K_c .

(b) On heating in a closed vessel PCl_5 dissociates into PCl_3 and Cl_2 . At 200°C the vapour density of the gaseous mixture is 75.5. Calculate the degree of dissociation of PCl_5 . ($P = 31$, $\text{Cl} = 35.5$)
Answer. (b) 0.3807

- 10.. Alcohol and acetic acid were mixed in equimolar proportions in aqueous medium at room temperature. At equilibrium 50% alcohol is converted into ester. Calculate how much ester will be formed if 2 moles of acetic acid and 1 mole of alcohol were mixed. **Answer. 0.67 mole**
11. At 25°C and 1 atm pressure the partial pressure in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and a total pressure of 5 atm. **Answer. 4.47 atm and 0.53 atm**

ELECTRO CHEMISTRY

❖ SOLUBILITY

- Find the degree of dissociation of HF in 1M aqueous solution. The value of K for the ionic equilibrium $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ is 7.2×10^{-4} .
- The solubility of CuBr is found to be 2.0×10^{-4} mol/l at 25°C . Calculate K_{sp} value for CuBr .
- Calculate the solubility of NiCO_3 in moles per litre and grams per litre. The value of K_{sp} for $\text{NiCO}_3 = 1.4 \times 10^{-7}$.
- . A 200 ml of 1.3×10^{-3} M AgNO_3 is mixed with 100 ml of 4.5×10^{-5} M Na_2S solution. Will precipitation occur ? ($K_{\text{sp}} = 1.6 \times 10^{-49}$)
- 50 ml of 6.0×10^{-3} M CaCl_2 is mixed with 30 ml of 0.04 M NaF . Will precipitation of CaF_2 occur ? (K_{sp} for $\text{CaCl}_2 = 4.0 \times 10^{-11}$)
- Calculate the solubility of silver chromate, Ag_2CrO_4 , in a 0.100 M solution of AgNO_3 . (K_{sp} for $\text{Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12}$)
- The solubility of lead sulphate in water 0.038 g lit $^{-1}$ at 25°C . Calculate its solubility product at 25°C . (molar mass of $\text{PbSO}_4 = 303$). **Answer. 1.5725×10^{-8}**
- When one litre of saturated solution of lead chloride, PbCl_2 is evaporated to dryness, the residue is found to weight 4.5 g. Calculate the value of K_{sp} for PbCl_2 . **Answer. 1.7×10^{-5}**
- The solubility product of AgCl in water is 1.5×10^{-10} . Calculate its solubility in 0.01 M NaCl solution. **Answer. 1.5×10^{-8} mol lit $^{-1}$**

10. Calculate the solubility product of AgCl if its solubility at 20 °C is 1.435×10^{-5} g/litre.
Answer. 1×10^{-10}
- 11.. Calculate the pH of 0.1 M CH₃COOH. The dissociation constant of acetic acid is 1.8×10^{-5} .
12. Find out the pH of a 0.002 M acetic acid solution if it is 2.3% ionised at this dilution.

❖ BUFFER SOLUTION

13. Find the pH of a buffer solution containing 0.20 mole per litre CH₃COONa and 0.15 mole per litre CH₃COOH. K_a for acetic acid is 1.8×10^{-5} .
14. Calculate the pH of a buffer solution that is 0.250 M in formic acid, HCOOH, and 0.100 M in sodium formate, HCOONa. K_a for formic acid is 1.8×10^{-4} .
15. The K_a of propionic acid is 1.34×10^{-5} . What is the pH of a solution containing 0.5 M propionic acid, C₂H₅COOH, and 0.5 sodium propionate, C₂H₅COONa. What happens to the pH of this solution when volume is doubled by the addition of water ?
16. 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 NH₄OH at the room temperature is 1.80×10^{-5} .
- 17.. The pH of a buffer solution containing 0.5 mole/litre of CH₃COOH and 0.5 mole/litre CH₃COONa has been found to be 4.76. What will be the pH of this solution after 0.1 mole/litre HCl has been added to the buffer ? Assume that the volume is unchanged. K_a = 1.75×10^{-5} .
- 18.. A litre of solution containing 0.1 mole of CH₃COOH and 0.1 mole of CH₃COONa provides a buffer of pH 4.74. Calculate the pH of solution after the addition of 0.02 mole NaOH. K_a = 1.8×10^{-5}
19. A chemist needs a buffered solution of propanoic acid, CH₃CH₂COOH, and its salt, CH₃CH₂COONa. Calculate the ratio [CH₃CH₂COOH]/[CH₃CH₂COONa] required to yield a pH of 4.30. K_a for propanoic acid is 1.3×10^{-5} .
20. Calculate the concentration of sodium formate, HCOONa, that must be present in a 0.10 M solution of formic acid to produce a pH of 3.80. K_a for formic acid is 1.8×10^{-4} .
- 21.. A chemistry student desires to prepare one litre of a solution buffered at pH 9.00. How many grams of ammonium chloride have to be added to one litre of 0.20 M NH₃ to make such a buffer. pK_b value of ammonia is 4.75 in the equation

SALT HYDROLYSIS

22. Define or explain the following terms :
- | | |
|-------------------------|--------------------------|
| (a) Anionic Hydrolysis | (b) Cationic Hydrolysis |
| (c) Hydrolysis constant | (d) Degree of Hydrolysis |
23. Sodium phenate is hydrolysed to the extent of 0.03% in 0.1 M aqueous solution at 25°C. Calculate
- (i) The hydrolysis constant of the salt; and

- (ii) the ionic product of water at 25°C. The dissociation constant of phenol is 1.3×10^{-10} at 25°C. **Answer. (i) 9×10^{-5} ; (ii) 1.17×10^{-14}**
24. A 0.02 M solution of sodium acetate in water at 25°C has a hydrogen ion concentration of 3×10^{-9} M. What is the hydrolysis constant of the salt? **Answer. 5.5×10^{-10}**
25. (a) What is hydrolysis constant of salt? Why aqueous solution of sodium carbonate is alkaline? Derive an expression for the hydrolysis constant and pH of this solution.
 (b) Calculate the pH of a decinormal solution of ammonium chloride. ($pK_a = 5.7$ and $pK_w = 14$) **Answer. 10.35**
26. The dissociation constant of acetic acid is 1.8×10^{-5} at 18°C. The ionic product of water is 10^{-14} at 18°C. What would be the degree of hydrolysis in a 0.012 N solution of sodium acetate? **Answer. 2.150×10^{-6}**
27. What is meant by the terms 'Degree of Hydrolysis' and 'Hydrolysis constant'? Deduce the relation between hydrolysis constant and the dissociation constant of the base in the case of the hydrolysis of a salt of a strong acid and a weak base.
28. (a) What is hydrolysis? Derive an expression for the hydrolysis constant of a salt of a weak acid and a strong base in terms of dissociation constant of a weak acid and ionic product of water.
 (b) Calculate the degree of hydrolysis of sodium acetate. Dissociation constant of acetic acid is 1.80×10^{-5} . Ionic product of water is 1×10^{-14} . **Answer. (b) 7.452×10^{-5}**
29. 20 ml of 0.2 M NaOH solution be treated with 40 ml of 0.2 M acetic acid solution to give 70 ml. Calculate the pH of the solution. **Answer. 4.5684**
30. Calculate the pH at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH. K_a for acetic acid is 1.9×10^{-5} . **Answer. 8.71**
31. 24. Calculate the percentage hydrolysis of sodium acetate in 0.1 N solution at 298 K, assuming the salt to be completely dissociated. (K_a for Acetic acid = 1.8×10^{-5}) **Answer. 0.0075%**
32. 25. What happens to the pH of 500 ml of solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 ml of 0.1 M NaOH is added ? **Answer. pH will increase**
33. What is the potential of a half-cell consisting of zinc electrode in 0.01M $ZnSO_4$ solution at 25°C, $E^\circ = 0.763$ V.

SOIL CHEMISTRY

1. A sample of clay surface soil is taken from a Bernadetha's farm and analyzed in the laboratory. The laboratory results indicate a CEC of the soil is 20cmol/kg and the following concentration of exchangeable cations: $Ca^{2+} = 3\text{cmol/kg}$, $Mg^{2+} = 4\text{cmol/kg}$, $Al_3^+ = 4\text{cmol/kg}$, $H^+ = 6\text{cmol/kg}$, and $K^+ = 3\text{cmol/kg}$. Calculate the percentage base saturation and percentage acid saturation.

2. A soil sample has cation exchange capacity of 25meq per 100g of soil. 20000mg of the soil were shaken with 40cm³ of 0.1M HCl. After filtering and washing the soil, the filtrate required 24cm³ of 0.1M NaOH for complete neutralization reaction. Calculate base saturation of the sample.
3. 10g of oven dry soil were shaken in 20cm³ of 0.1M hydrochloric acid solution. The mixture was then filtrated and the soil thoroughly washed in distilled water, the filtrate and washings were neutralized by 12cm³ of 0.1M sodium hydroxide. If the total cation exchangeable capacity of the soil is 25meq/100g of oven dried soil. Calculate the percentage base saturation of the soil and percentage acid saturation.
4. A soil test shows the following Nutrient meq/100g soil Ca²⁺ 2.1 Mg²⁺ 2.0 K⁺ 9.9 Al³⁺ 7.6 NH₄⁺ 0.6 Na⁺ 0.1
 - (a) Calculate the CEC of the soil
 - (b) Calculate the percentage base saturation of the soil
 - (c) Calculate the percentage aluminium saturation of the soil.
5. A soil sample of 30g was analyzed and found to contain 0.0045g of Mg. what is the concentration of calcium in the soil in mill equivalent per 100g of soil?
6. The exchangeable hydrogen from 70g of oven dry soil was neutralized with 120cm³ of 0.1M NaOH. If the total CEC of the soil is 30meq/100g of the soil. Calculate:-
 - i. Percentage base saturation of the soil sample
 - ii. The concentration of H⁺ ions (in meq) in 80g of the dry soil above
 - iii. Comment on the nature of the soil above in (b) (i) above.
7. Calculate the neutralizing value of calcium silicate (CaSiO₃)
8. Calculate the amount of Calcium carbonate required to lime an acidic soil that requires 100g of calcium oxide for the same
9. Water was added to 100g of soil to make a 200cm³ soil solution. If this soil solution requires 0.0074g of calcium hydroxide for neutralization. What is the pH of this solution?
10. The neutralizing value of calcium carbonate, CaCO₃ is 109%. Calculate the grams of CaCO₃ equivalent to 100g of a given liming materials.
11. A piece of land requires 120kg of N to be applied per hectare so as to fulfill plant requirements of nitrogen. Calculate, in kilograms, the quantity of ammonium sulphate fertilizer which contains 21% of Nitrogen (N) required to meet this demand.
12. Rebecca was advised to supply 160kg of N to her maize farm. Calculate the mass of fertilizer (of 80% by mass Ca(NO₃)₂) which has to buy to meet the requirements.

13. A certain soil requires 80 Kg of N per hectare so as to fulfill plant requirements of nitrogen. Calculate, in kilograms, the quantity of ammonium sulphate fertilizer required to meet this demand.
14. A farm requires 120kg of nitrogen. What is weight of urea fertilizer labeled 37-0-0 needs to be applied to the soil to meet this demand? Show clearly how you obtain your answer.
15. (a) State the meaning of the following terms
 - (i) Soil colloids
 - (ii) Ion exchange
 (b) (i) Explain why nitrate is more leached from the soil than ammonium
 (ii) Explain why sandy soils have zero C.E.C
 (c) (i) What is C.E.C?
 (ii) Give three significance of C.E.C
 (d) Water was added to 100g of soil to make a 200cm³ soil solution. If this soil solution requires 0.0074g of Ca(OH)₂ for neutralization. What is the PH of this soil solution.
16. (a) Define the following terms as used in soil chemistry
 - (i) Colloidal state
 - (ii) Cation exchange capacity
 - (iii) Percentage base saturation
 (b) (i) Briefly explain two methods used to measure soil pH
 (ii) Explain the major sources of negative charges on the surface of soil colloids?
 (iii) Outline the general characteristics of phosphatic fertilizers
 (c) 10g of oven dry soil were shaken in 20cm³ of 0.1M hydrochloric acid solution. The mixture was then filtrated and the soil thoroughly washed in distilled water, the filtrate and washings were neutralized by 12cm³ of 0.1M sodium hydroxide. If the total cation exchangeable capacity of the soil is 25meq/100g of oven dried soil. Calculate the percentage base saturation of the soil
17. 20 g of soil sample was shaken with 40 cm³ of 0.1 M HCl solution. After filtering and washing the soil, the filtrate required 27 cm³ of 0.1 M NaOH solution for complete neutralization. The total Cation Exchange Capacity (CEC) of the soil is 29 milli.Eq per 100 g of the soil sample. Calculate the Percentage Base Saturation (PBS) of the soil sample.

ORGANIC CHEMISTRY

1. (a) Define the following terms;
 - (i) Functional group.
 - (ii) Chain isomerism.

(b) The following names are incorrect according to IUPAC system. Give the structural formula and correct names as per IUPAC.

(i) 3 – methylbutane.

(ii) 2 – propylbut – 2 – ene.

(iii) 2 – isopropylpropane.

(iv) 1 – ethyl – 2, 2 – dimethylpropane.

(c) Alkanes are obtained by processing crude oil.

(i) Explain why different alkanes in crude oil can be separated by fractional distillation?

(ii) By using molecular formula, complete the equation for the cracking of octane to produce ethane and only one other organic compound. Give at least two possible equations.

2. (a) Why benzene though highly unsaturated, it does not undergo addition reactions? Briefly explain.

(b) Arrange the following set of compounds in order of decreasing reactivity toward methenium ion (H_3C^+);

(i) Benzene, 4-nitrotoluene and 4-chlorophenol.

(ii) Isopropylbenzene, carboxybenzene and chlorobenzene.

(c) Briefly explain the following phenomenon;

(i) Hydrogenation in benzene occurs at higher temperature than in hexene.

(ii) Nitration of aminobenzene gives significant amount of meta product although the amino group in benzene is ortho - para director.

(d) With the help of chemical reactions, show how the following compounds can be prepared from ethanol as the source of carbon atoms;

(i) Benzene. (ii) Ethylbenzene.

3. (a) Give a chemical test to distinguish the followings;

(i) Methyl methanoate and methyl ethanoate.

(ii) N-methylethanamine and N,N-di methylethanamine.

(b) Give reason(s) for each of the following:

(i) Phenylamine undergoes nitration more readily than benzene carbaldehyde.

(ii) Propanone does not give positive iodoform test but propan-1-ol does

. (iii) Propanone is less readily attacked by nucleophile than propanal.

(c) An organic compound P was boiled with dilute H_2SO_4 to produce an acid Q which was monobasic. Q was esterified with ethanol to give an ester R of molecular mass 150. Compound Q can undergo reduction to form S. Give the structural formula for P, Q, R and S.

(d) With an example, define the following terms;

(i) Aldol-ketol condensation reaction

(ii) Cannizaro reaction. (2 Marks)

4. Give the structure(s) of monomer which gives the following polymer in polymerisation;
 - (i) Dacron.
 - (ii) Nylon-6,6.
 - (iii) Polystyrene.
- (c) (i) Give the structure of repeating unit in terylene and state the type of polymerization involved during its formation.
 - (ii) Give the structure of repeating unit in poly(phenylethene) and state the type of polymerisation involved during its formation.
 - (iii) Explain why dilute sodium hydroxide will cause holes to appear in clothing made from polymers such as terylene but a poly(phenylethene) container can be used to store sodium hydroxide?
- (d) With reasons, write down the use of the following polymers:
 - (i) Butyl-rubber.
 - (ii) Polyhaloalkene.
 - (iii) Polyacrylonitriles.
- (e) Briefly explain the vulcanisation of rubber under the following considerations
 - (i) Meaning.
 - (ii) Importance and its application
5. (a) (i) By using the chemical equation explain why tertiary halo alkane cannot undergo SN2 reaction mechanism
 - (ii) Benzene is more reactive than nitrobenzene while methylbenzene is more reactive than benzene. Explain this observation.
6. (a) When 1,2-dibromodecane was treated with potassium hydroxide in aqueous ethanol, it yields a mixture of three isomeric compounds of molecular formula $C_{10}H_{19}Br$. Each of these compounds was converted to dec-1-yne on reaction with sodium amide in dimethyl sulphoxide. Identify the three compounds.
 - (b) Explain briefly the preparation of acetylene (ethyne) by; -
 - i. Pyrolysis of natural gas.
 - ii. Action of water on calcium carbide.

03. a) An aromatic compound D (C_8H_8O) give a positive result with 2,4 dinitro – phenyl hydrozone but gives yellow precipitate of compound E treatment with iodine and sodium solution. Compound D give negative Tollens or Fehling test. On drastic oxidation with $KMnO_4$ forms a carboxylic acid F ($C_7H_6O_2$) which is also formed along with the yellow compound in the above reaction. Identify the structure D, E, and F also write all chemical reaction involved.

(b) A compound A of Molecular formula of $C_3H_7O_2N$ On reaction with iron and concentrated hydrochloric acid give the compound B of molecular formula C_3H_8O . Compound C Gives Effervescence with sodium on oxidation with CrO_3 compound C given saturated aldehyde containing three carbonic atoms deduce the structure of A, B and C

INORGANIC CHEMISTRY

1. (a) Aluminium oxide is said to be amphoteric. Explain this fact by aid of chemical equation.
(b) Iron III carbonate never exists. Explain this statement
(c) Explain the following with the aid of chemical reaction if applicable.
 - i. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ when heated can never give out anhydrous MgCl_2
 - ii. CuCl_2 solution is acidic to litmus paper
 - iii. Fe_3O_4 is called mixed oxide.
2. (a) (i) Generally extraction of metals from their ores involves four stages. Obtaining the ore, concentrating the ore, concentrating the compound of interest in the ore, chemical reduction and refining of the crude metal. Describe how Aluminium is extracted from its ore basing on these stages.
(ii) Show that the properties of aluminium suit its wide range use.
(b) Transitional elements show a variety of behaviours. With vivid example explain five (05) properties shown by such metals.
(c) Give the IUPAC name of the following
 - i. $[\text{Cr}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$
 - ii. $[\text{CoCl}(\text{NO}_2)(\text{en})_2]^+$
 - iii. $\text{K}_4[\text{Fe}(\text{CN})_6]$
 - iv. $[\text{FeBr}_2(\text{H}_2\text{O})_4]^+$
 - v. $[\text{CoCl}_2(\text{NH}_3)_4]_3 [\text{Cr}(\text{CN})_6]$
3. (a) What do you understand by the term deliquescence? Explain what makes a hydrated salt to deliquescence.
(b) List down at least three useful applications of sulphates. Give at least one example for each.
(c) With the help of chemical equation(s), explain the followings;
 - (i) Brown ring test.
 - (ii) A test to distinguish sodium carbonate and sodium bicarbonate.
4. (a) Explain the following observations:
 - (i) Oxidizing power of halogens decreases on descending the halogen group.
 - (ii) Reducing power of hydrogen halides increases on descending the halogen group.
(b) With help of chemical equations, explain each of the followings;
 - (i) Strontium does not react with dilute sulphuric acid but it reacts when the acid is concentrated.
 - (ii) Among earth metals, only beryllium reacts with dilute sodium hydroxide.
 - (iii) Beryllium oxide is amphoteric while other oxides of earth metals are basic.
 - (iv) Silver chloride dissolves in the ammonia solution while silver bromide does not.
(c) Explain the general trends in physical properties of elements across the period and down the group by considering;

- (i) Atomic size.
 - (ii) Electron affinity.
 - (iii) Electronegativity.
 - (iv) Ionization energy.
5. (a) With the aid of chemical equation explain the preparation of metallic hydroxides by:
- (i) Direct method
 - (ii) Indirect method
- (b) State two (2) uses of CaSO_4 in real life and the characteristics that make CaSO_4 suitable for those uses.
- (c) A salt A when heated give black solid and colourless irritating gas that turn dichromate paper orange to green. A solution of salt A give reddish brown precipitate with potassium Hexacyanoferrate (II). Identify the salt A and write the two balanced equation when heated and when reacted with potassium Hexacyanoferrate (II)

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