

CEMA-CC-4-9-TH: PHYSICAL CHEMISTRY 3

The enlisted Questions are not exhaustive, only suggestive. Please additionally consult the Chapter End Exercises of your Text Books as recommended in the Syllabus and also the previous year question papers of the University.

Foundation of Quantum Mechanics

1. Photoelectric work function and ionization potential of a metal are not the same--- Comment.
2. In a photoelectric experiment when the emitter metal is irradiated with light of two different frequencies and the following observations were made:
 - a. Electrons could not be emitted by using very intense beam of light having wavelength λ
 - b. Electrons could be easily emitted using a weakly intense beam of wavelength λHow do you explain the phenomena? Which wavelength is shorter?
3. What happens to the energy of the photon when the absorbed energy is insufficient to allow the electron to escape from the metal surface?
4. What is the energy in joules and electron volts of a photon of 420-nm violet light?
5. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the binding energy (or work function) of electrons for calcium metal is 2.71 eV?
6. Write notes on
 - a. Steffan-Boltzman law
 - b. Wien's displacement law indicating the quantities involved
7. How many photons are present in 1 cm³ of radiation in thermal equilibrium at 500K? Find the wavelength at which the energy density of radiation is maximum.
8. Assuming that you're a source of Blackbody radiation, determine the peak wavelength of light you are emitting. In what region of the spectrum is your peak wavelength?
9. The Compton effect is not observed when visible light photons scatter from the electrons in a material-Justify or criticize.
10. Can you explain the origin of the Compton scattered radiation which has the same frequency as the incident radiation?
11. An incident 71-pm X-ray is incident on a calcite target. Find the wavelength of the X-ray scattered at 30o angle. What is the largest shift that can be expected in this experiment?
12. Make use of de Broglie relationship to calculate total energy of H-atom in the Bohr model, where the radius is assumed to be equal to a_0 .
13. How does the de Broglie hypothesis lead to one important postulate made by Bohr in his theory of the hydrogen atom.
14. Calculate the wavelength of a 100-gram ball moving with velocity of 36 km/hr. Also calculate the wavelength of an electron of mass 9.1×10^{-31} kg with a velocity of 107 ms⁻¹. In which case consideration of wave behaviour is meaningful.
15. State Wilson-Sommerfeld quantization rule.
16. Apply Wilson-Sommerfeld quantization rule to obtain an energy expression for a particle in one dimensional box.
17. Explain Bohr correspondence principle, taking the case of H atom.

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18. What is the de Broglie wavelength of the cricket ball of 0.145 kg thrown at speed 48.325 m/s? Assuming the uncertainty in the measured speed was 5.5×10^{-28} m/s, what was uncertainty in the ball's position as it passed the batsman? Did the fact that the ball had wavelike properties add significantly to the challenge of hitting that ball?
19. Explain the terms: linear operator, eigenvalue and stationary state
20. Prove that Hermitian operator gives us real eigenvalues.
21. Show that momentum operator is a Hermitian operator.
22. If the relative uncertainty in the velocity of a proton in the Large Hadron Collider is 3.0%, what is the uncertainty in its position? How does this uncertainty affect the ability of scientists to collide such a proton with an atom (diameter roughly on the order of Angstroms, or 1×10^{-10} m) or another proton (charge radius about 0.9 fm) in the Large Hadron Collider?
23. What do wave functions (Ψ) tell you? Determine, citing reason, whether each of the following functions is acceptable or not as wave function over the indicated intervals.
 - a. e^{-x} (0, ∞)
 - b. e^{-x} ($-\infty$, ∞)
 - c. e^{-x^2} ($-\infty$, ∞)
 - d. $1/x$ (0, ∞)
 - e. $\sin^{-1}x$ (-1, 1)
 - f. $e^{-i\phi}$ (0, 2π)
 - g. $\tan x$ (0, π)
24. Expand the operator $d/dx + x^2$.
25. Test whether the following functions are eigenfunctions of the operator d^2/dx^2 write also the corresponding eigenvalues.:
 $\sin x$, $\sin x \cos x$, $A \sin mx + B \cos nx$
26. An operator \hat{A} is defined as: $\hat{A} = x d/dx$, find \hat{A}^2 .
27. Show that if two operators commute, they have simultaneous non-degenerate eigenfunctions.
28. For a particle in a box problem, show that the energy levels are continuous, if either the mass of the particle or length of the box become large.
29. Show that the error in de Broglie wavelength (λ) is related to the error in velocity (v) by the relation $d\lambda = -\lambda dv/v$.
30. A cubic box with each side measuring 10 \AA (with zero potential inside and infinite potential outside) contains a system of 4 quantum particles. Find the degeneracy of the lowest energy state of the system.
31. Calculate the probability of finding a particle moving freely in an one dimensional box of length l within the distance $l/2 \pm l/10$ when the particle is present in ground state.
32. A particle of mass m moves freely in a one-dimensional box which has zero potential in the region $|x| < a$, and infinite outside this region.
 - a. Derive expressions for normalised solutions of the Schrodinger equation and the corresponding energies.
 - b. Sketch the wave functions for the four lowest energies. What are the parities of the wavefunctions?

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Crystal Structure

1. What is a crystal lattice? What is a Unit Cell? Name all possible types of crystal systems? 2
 2. State and explain the 1st laws of crystallography. 2
 3. What is crystal polymorphism? Give examples. 2
 4. What are the crystal habits? 2
 5. What are fcc, bcc and hcp lattices? 2
 6. What are Miller Indices and why these are important in crystallography? 2
 7. What are tetrahedral and octahedral voids? 2
 8. Explain why in a tetragonal system face centred Bravais lattice is excluded? 2
 9. Explain why only x-rays are suitable for the determination of crystal structure? 2
 10. Why five-fold or higher axis of rotation cannot exist in a crystal? 2
 11. How many symmetry axes and planes are present in a simple cubic and in a tetrahedral arrangement of crystals? 4
 12. Calculate the number of units per unit lattice in fcc, bcc and hcp arrangements. 2
 13. A certain metal crystallises both in fcc and bcc lattices. Which one will be denser and why? 2
 14. Compare the void spaces in a fcc and a bcc arrangement of a crystal. 2
 15. Why KCl appears to be a cubic lattice system in x-ray crystallographic study when it actually has a fcc lattice? 2
 16. CsCl has bcc arrangement and its unit cell edge length is 400 pm, calculate the interionic distance in it. 2
 17. Draw the (111) and (222) planes in a simple cubic unit cell, with lattice constant 'a'. Determine the normal distance between the two planes. 2
 18. The distance between (111) planes in a fcc crystal is $2A^0$. Determine the lattice parameter and atomic diameter. 2
 19. Calculate the angle between the [110] direction and the [111] direction for a monoclinic lattice with $a = 0.3 \text{ nm}$, $b = 0.4 \text{ nm}$, $c = 0.5 \text{ nm}$, and $\beta = 107^\circ$. 2
 20. A crystal plane cuts intercepts of a , $b/2$ and $3c/2$, along the x , y , z directions. Determine the Miller indices of the plane. 2
 21. Consider x-ray diffraction from a crystal with fcc lattice. Find out the lattice plane for which there will be no diffraction peak: (212), (111), (200) or (311)? 2
 22. The first order reflections from the (100), (110) and (111) planes of a given cubic crystal of NaCl were found to occur at 5.9° , 8.4° , and 5.2° respectively. Determine the type of cubic lattice to which the crystal belongs? 2
 23. Show that Dulong-Petit's law is a special case of Einstein equation for heat capacity of solids. 2
 24. What are the Einstein Temperature and Debye temperature of a Solid? 2
 25. How the Einstein Temperature differs from the Debye temperature of a Solid? 2
 26. For the two solid systems, x and y , following experimental data are collected: 4
- | | x | y |
|-------------------------------------|-------|--------|
| edge length (pm) | 286 | 388 |
| density (gmcm^{-3}) | 7.86 | 12.16 |
| molar mass (gmmol^{-1}): | 55.85 | 106.40 |
- Evaluate the type of cubic lattice to which each of the systems belongs.
27. A metal of atomic mass 55 crystallises in fcc lattice with edge of the unit cube as 0.5 nm. Determine the density of the metal. 4
 28. A metal of density 10.5 and atomic mass 108 crystallises in fcc. Assuming that the atoms are in contact, determine their radius. 4

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29. Polonium forms a simple cubic crystal with one atom in the basis. The lattice constant is 3.359 Å. The density of Po is 9.23 g/cm³. How many unit cells are there in 100 g of polonium? 4
30. A metal has an fcc crystal structure. The lattice constant is 0.38 nm and the atomic weight of the atoms is 85. The lattice constant is the length of the conventional (cubic) unit cell. The mass of an atom is the atomic weight times the atomic mass constant $u = 1.6605402 \times 10^{-27}$ kg. What is the density of this metal? What is the distance between neighbouring atoms? 4

Application of Thermodynamics-II

Colligative Properties

1. What is the origin of the colligative properties of a solution 2
2. From the μ v/s T diagram justify that ΔT_f is greater than ΔT_b for a solution of a non-volatile solid. 2
3. Explain, whether ebullioscopic constant and cryoscopic constant are the properties of the solvent or solute in a solution? 2
4. When 1.00 g of urea [CO(NH₂)₂] is dissolved in 200 g of solvent A, the A freezing point is lowered by 0.250°C. When 1.50 g of the nonelectrolyte Y is dissolved in 125 g of the same solvent A, the A freezing point is lowered by 0.200°C. (a) Find the molecular weight of Y. (b) The freezing point of A is 12°C, and its molecular weight is 200. Find $\Delta_{fus}H_m$ of A. 4
5. Calculate the ebullioscopic constant for water if its enthalpy of vaporization is 40.685 kJ mol⁻¹. 2
6. A solution of sucrose (molar mass = 342 g mol⁻¹) is prepared by dissolving 68.4 g in 1000 g of water at 293 K. What is the: (i) Vapour pressure (ii) Osmotic pressure (iii) Boiling point (iv) Freezing point of the solution. Given vapour pressure of water at 293 K is 17.5 mm, $K_b = 0.52$ K kg mol⁻¹, $K_f = 1.86$ K kg mol⁻¹. 4
7. What does vant Hoff 'i' factor signifies? 2
8. 0.1 M solution of KNO₃ has an osmotic pressure of 4.5 atm at 300 K. Calculate apparent degree of dissociation of the salt. 4
9. Why equimolar solution of sucrose and sodium chloride solutions in water are not isotonic? 2
10. A 4% solution of sucrose is isotonic with 3% solution of an unknown organic substance. Calculate the molar mass of the unknown substance. 2
11. Discuss the method of determining the molar mass of a non-volatile solute by any of the colligative properties of the solution of the solute? Measurement of which colligative property is most suitable in the determination of the molar mass of a non-volatile solute and why? 4
12. A Stream of dry air was passed through a bulb containing a solution of 7.50 g of an aromatic compound in 75.0 g of water and through another globe containing pure water. The loss in mass in the first globe was 2.810 g and in the second globe it was 0.054 g. Calculate the molecular mass of the aromatic compound. (Molar mass of water = 18) 4
13. Osmotic pressure of an aqueous solution of sucrose at 303 K is 2.47 atm.; the molar volume of water at this temperature is 18.10 cm³. Calculate elevation of boiling point of this solution. Given $\Delta H_{vap} = 539$ cal g⁻¹. 4
14. The melting point of Phenol is 40.00°C. A solution containing 0.172 gm of acetanilide (C₈H₉ON) in 12.54 gm Phenol freezes at 39.25 °C. Calculate Cryoscopic Constant (K_f) and Latent Heat of Fusion for Phenol. 4
15. How much urea (in gms) must be dissolved in 10⁻² m³ of water to yield a solution whose osmotic pressure will be 2.03 x 10⁵ Nm⁻² at 27°C? 2
16. The osmotic pressure of an aqueous solution of urea at 300 K is 120 kPa. Calculate the freezing point of the same solution. 2

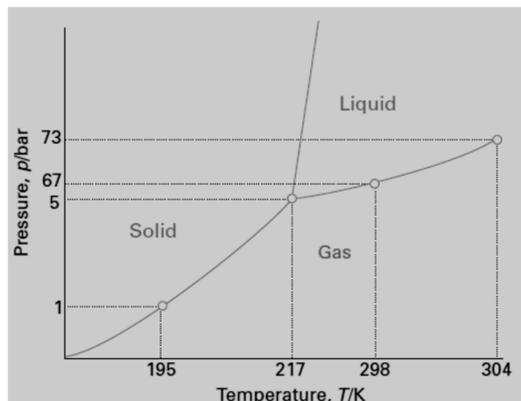
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Phase Equilibrium

1. Show that the slope of μ v/s T curves for the solid \leftrightarrow Liquid \leftrightarrow Gas equilibrium follows the order: $(\partial \mu / \partial T)_{T^{\text{Solid}}} > (\partial \mu / \partial T)_{T^{\text{Liq}}} > (\partial \mu / \partial T)_{T^{\text{Gas}}}$ 2
2. Using Clapeyron equation construct and explain the phase diagram (P v/s T) of water system (one component) involving equilibrium transition between all three phases. 4
3. For Liquid \leftrightarrow Vapour equilibrium transformation, derive the form of Clausius-Clapeyron equation. How do we determine the value of enthalpy of vaporisation (ΔH_{vap}) and the boiling temperature (T_b) using the equation? 4
4. Compare the characteristics of 1st and 2nd order phase transitions? 2
5. Define boiling point of a liquid and melting point of a solid. 2
6. On what factors does the sign of the slope dP/dT of solid to liquid transformation depends? 2
7. Explain why sublimation has a positive slope in the phase diagram of water? 2
8. Explain why fusion curve of ice has a negative slope? 2
9. The enthalpy of vaporisation of water is $40.69 \text{ KJ mol}^{-1}$, the molar volume of liquid water is $0.019 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$ and the molar volume of steam is $30.199 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ all at 100°C and 1 atm. Calculate the rate of change in boiling point of water at 100°C and 1 atm pressure. 4
10. If the enthalpy of vaporisation of water is assumed to be constant at 2255 KJ g^{-1} , calculate the temperature at which water will boil under a pressure of 77.0 cm of Hg, the boiling point of water being 373.05 K at 76.0 cm Hg. The specific volume of water vapour at 373.15 K at 76.0 cm Hg is $1644 \text{ cm}^3 \text{ g}^{-1}$ and that of liquid water is $1 \text{ cm}^3 \text{ g}^{-1}$. 4
11. Water boils at 373K at one atmospheric pressure. At what temperature will it boil when atmospheric pressure becomes 528 mm of Hg at some space station? (Latent heat of water = 2.28 kJ g^{-1}) 4
12. What is the difference between triple point and the freezing point? 2
13. The vapour pressure of solid and liquid white phosphorous are given by the expressions: $\log(p_2/\text{atm}) = -(2875\text{K}/T) + 5.36$ and $\log(p_1/\text{atm}) = -(2740\text{K}/T) + 4.95$ respectively. Calculate (a) the temperature and pressure of the triple point of phosphorous and (b) the molar enthalpy and molar entropy of fusion of phosphorous at the triple point. 4
14. What is Trouton's rule and how far it is being obeyed by liquid systems? 2
15. The vapour pressure of a liquid which obeys Trouton's rule rises by 5.2 KPa between temperatures 1 K below and 1 K above the normal boiling point. Determine the value of normal boiling point and molar enthalpy of vaporisation of liquid. 4
16. The vapour pressure of water at 303.15K is 0.0424 bar when exposed to an insoluble gas at 1.01325 bar pressure. What will be the vapour pressure if the gas pressure were increased to 101.325 bar? Density of water is 0.996 gcm^{-3} and it may be assumed to be incompressible. 4
17. How many phases and components are present in the following systems: (i) CCl_4 mixed with water (ii) water and alcohol (iii) CaCO_3 , CaO and CO_2 . 2
18. Compute the number of components in the following system: a solution containing Na^+ , Cl^- , Ag^+ , NO_3^- , AgCl(s) and water. 2
19. Why four phases of a one component system (i.e. Sulphur) does not exist at equilibrium? 2
20. If we start with pure ice in a sealed container at (i) 1 atm and at (ii) 2 atm and increase the temperature of the system, what will we observe? 2
21. Show that Chemical Potential of a substance present in more than one phase in equilibrium with each other has the same value in all phases. 2
22. Explain the main differences between the phase diagram of CO_2 and water system. 4

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23. Use the phase diagram in Figure below to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K is subjected to the following cycle:
 (a) constant-pressure heating to 320 K, (b) isothermal compression to 100 atm, (c) constant-pressure cooling to 210 K, (d) isothermal decompression to 1.0 atm, constant-pressure heating to 298 K.



24. What is supercooled water? Why is it called a metastable state? 2
25. Explain in a phase diagram polymorphism (allotropy) shown by sulphur system. 4
26. What is dry ice? Is it possible to get dry ice at atmospheric pressure? 2
27. Why a three-dimensional model of phase diagram is needed for two-component systems? How is this difficulty overcome by reduced phase rule equation? 2
28. Addition of a solute at constant T and P to a pure solvent A always decreases μ_A . Explain? or Addition of a non-volatile solute to a pure solvent at constant T always lowers the vapor pressure. Explain? 2
29. Explain why a real solution deviates from ideal behaviour as the mole fraction of the solute dissolved in it is increased? 2
30. The vapour pressure of pure components A and B are 120 mm and 96 mm of Hg. What will be the partial pressures of the components and total pressure when the solution contains 1 mole of component A and 4 mole of component B and the solution is ideal? What will be the composition of the vapour phase? 4
31. Show that Henry's law is a special case of Raoult's law. 2
32. State limitations of Henry's law? 2
33. Solubility of pure oxygen in water at 20°C and 1 atm pressure is 1.38×10^{-3} mole/litre. Calculate the concentration of oxygen at 20°C and partial pressure of 0.2 atm. 2
34. Define an ideal solution thermodynamically. What is a non-ideal solution? 2
35. Draw and explain the vapour pressure-composition diagram showing positive deviation from Raoult's law. Why do positive deviations occur? 4
36. What is the maximum number of phases that can coexist in a binary system? 2
37. State Konowaloff's rule and derive it from Duhem-Margules equation. 4
38. What are partially miscible liquids? Show that the compositions of two conjugate solutions in the miscible gap are quite definite for a given temperature and are independent of the relative amounts of the two solutions. 4
39. Draw a schematic plot connecting the compositions of two conjugate solutions at different temperatures. What is CST and show that CST is a nonvariant point? 4
40. Under what circumstances a liquid pair shows both the upper and the lower CST? 2
41. What effect impurities have on CST? 2
42. Water and phenol are partially miscible at 50°C. When these two liquids are mixed at 50°C and 1 atm, at equilibrium one phase is 89% water by weight and the other is 37 % water by weight. If 6.00 g of phenol and 4.00 g of water are mixed at 50°C and 1 atm, find the mass of water and the mass of phenol in each phase at equilibrium by using (a) the lever rule; (b) conservation of matter (without using the lever rule). 4

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43. State the Nernst distribution law. Derive the following modified form of it for a solute S having normal existence in the liquid A and dimerises in liquid B: 4
 $[S]_A / ([S]_{B, \text{total}})^{1/2} = \text{constant}$
44. The distribution coefficient of I_2 is measured between aqueous solution of NH_4Cl and Chloroform. Will there be any difference if the same is being studied between pure water and chloroform? 2
45. Describe how distribution experiment can be used to determine the equilibrium constant of the reaction: $KI + I_2 \leftrightarrow KI_3$. 4
46. Show that multi stage solvent extraction is more profitable than the single stage solvent extraction. 2
47. Justify or criticize the statement: A liquid solution of two substances will always freeze entirely at one temperature. 2
48. When 2 g of a non-volatile hydrocarbon containing 94.4 % carbon is dissolved in 100 g Benzene, the vapour pressure of Benzene at $20^\circ C$ is lowered from 0.09954 bar to 0.09867 bar. Calculate molecular formula of hydrocarbon. 4
49. Show that if Raoult's law is applicable to one of the constituents of a binary liquid mixture, at all compositions, it must be equally applicable to the other constituent 4
50. Calculate the concentration of carbon dioxide in fat given that the Henry's law constant is 8.6×10^4 Torr and the partial pressure of carbon dioxide is 55 kPa. 2
51. The vapour pressure of a solution containing 6.69 g of $Mg(NO_3)_2$ dissolved in 100g of water is 7.47 kPa at 373 K. Calculate degree of dissociation of salt in solution. 2
52. Estimate the vapour pressure of seawater at $20^\circ C$ given that the vapour pressure of pure water is 2.338 kPa at that temperature and the solute is largely Na^+ and Cl^- ions, each present at about 0.50 mol dm^{-3} . 4
53. Methyl ethyl ketone and water are partially miscible. At 303 K the two layers contain 21.9 and 89.9 % by mass of Methyl ethyl ketone. What will be mass of each layer when 50 g each of Methyl ethyl ketone and water are equilibrated at this temperature? (Ans: 41.3g of Methyl ethyl ketone) 4

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