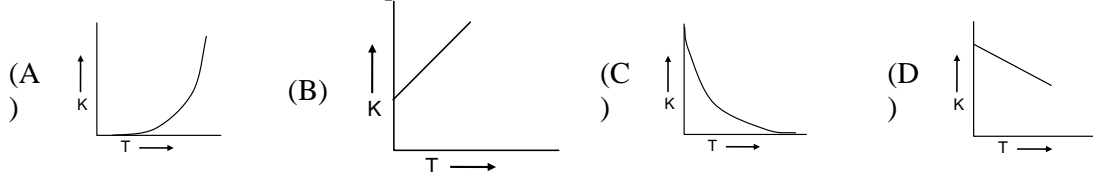


PHYSICAL CHEMISTRY

1. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **JEE-2010**



1. **A**  
 $K = Ae^{-E_a/RT}$   
 Rate constant increases with increase in temperature exponentially.

2. The species which by definition has ZERO standard molar enthalpy of formation at 298 K is **JEE-2010**

(A) Br<sub>2</sub>(g)                      (B) Cl<sub>2</sub>(g)                      (C) H<sub>2</sub>O(g)                      (D) CH<sub>4</sub>(g)

2. **B**  
 The standard molar enthalpy of formation of elements in standard state is zero. For chlorine standard state is gas.

3. The bond energy (in kcal mol<sup>-1</sup>) of a C–C single bond is approximately **JEE-2010**

(A) 1                      (B) 10                      (C) 100                      (D) 1000

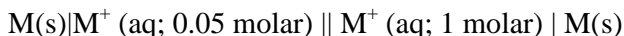
3. **C**

4. Among the following, the intensive property is (properties are) **JEE-2010**  
 (A) molar conductivity                      (B) electromotive force  
 (C) resistance                      (D) heat capacity

4. **A, B**  
 Molar conductivity and EMF are physical quantities independent of amount of matter in the system.

**Paragraph for Questions 5 to 6**

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is : **JEE-2010**



For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70 \text{ mV}$ .

5. For the above cell  
 (A)  $E_{\text{cell}} < 0; \Delta G > 0$     (B)  $E_{\text{cell}} > 0; \Delta G < 0$     (C)  $E_{\text{cell}} < 0; \Delta G^\circ > 0$     (D)  $E_{\text{cell}} > 0; \Delta G^\circ < 0$
6. If the 0.05 molar solution of M<sup>+</sup> is replaced by a 0.0025 molar M<sup>+</sup> solution, then the magnitude of the cell potential would be  
 (A) 35 mV                      (B) 70 mV                      (C) 140 mV                      (D) 700 mV

5. **B**  
 $E = E^\circ - \frac{2.303 RT}{nF} \log_{10} Q$   
 Here temp is not given

$$E = 0 - \frac{2.303 RT}{nF} \log_{10} \frac{.05}{1}$$

So  $E = 70 \text{ mV}$ .

$$\Delta G = -nFE$$

Here  $E_{\text{cell}}$  is +ve then  $\Delta G$  is negative.

6. **C**

When  $E^\circ = 0$

$$\frac{E_1}{E_2} = \frac{\log_{10} Q_1}{\log_{10} Q_2}$$

$$\frac{70}{E_2} = \frac{\log_{10} .05}{\log_{10} (.05)^2}$$

$$E_2 = 140 \text{ mV}$$

7. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is **JEE-2010**

7. **3**

$$\text{Average titre value} = \frac{25.2 + 25.25 + 25}{3} = 25.15$$

The minimum digits after decimal in data decides the extent of significant digit after decimal in "average value". Hence answer is 25.1 with total no. of significant digits = 3.

8. The concentration of R in the reaction  $R \rightarrow P$  was measured as a function of time and the following data is obtained : **JEE-2010**

<b>[R] (molar)</b>	1.0	0.75	0.40	0.10
<b>t(min.)</b>	0.0	0.05	0.12	0.18

The order of the reaction is

8. **0**

<b>t(min.)</b>	<b><math>[R]_0 - [R]_t</math></b>	<b><math>\frac{[R]_0}{[R]_t/\Delta t}</math></b>	<b>-</b>
0.05	0.25	5	
0.12	0.60	5	
0.18	0.9	5	

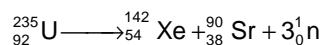
since,  $\frac{[R]_0 - [R]_t}{\Delta t}$  ratio is constant. This indicates that the given reaction is of zero order.

For zero order reactions,

$$K = \frac{1}{\Delta t} ([R]_0 - [R]_t)$$

9. The number of neutrons emitted when  ${}_{92}^{235}\text{U}$  undergoes controlled nuclear fission to  ${}_{54}^{142}\text{Xe}$  and  ${}_{38}^{90}\text{Sr}$  is **JEE-2010**

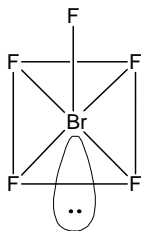
9. **3**



No. of neutrons emitted = 3

10. Based on VSEPR theory, the number of 90 degree F-Br-F angles in  $\text{BrF}_5$  is **JEE-2010**

10. **0**

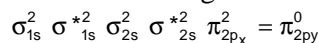


Because LP–BP repulsions are stronger than BP–BP repulsions, there will be a distortion in the geometry & bond angles deviate from regular  $90^\circ$ .

11. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule  $B_2$  is **JEE-2010**

- (A) 1 and diamagnetic (B) 0 and diamagnetic  
(C) 1 and paramagnetic (D) 0 and paramagnetic

11. **A**  
Electronic configuration of ' $B_2$ ' is



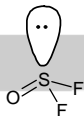
Number of unpaired electrons = 0  $\Rightarrow$  diamagnetic

$$\text{Bond order} = \frac{n_{bo} - n_{abo}}{2} = \frac{4 - 2}{2} = 1$$

12. The species having pyramidal shape is **JEE-2010**

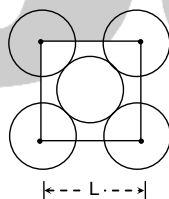
- (A)  $SO_3$  (B)  $BrF_3$  (C)  $SiO_3^{2-}$  (D)  $OSF_2$

12. **D**



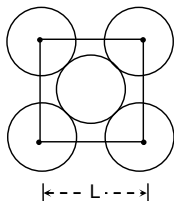
Central atom ' $S$ ' has 3  $\sigma$  bond pairs and 1  $\uparrow p$  of electrons.

13. The packing efficiency of the two-dimensional square unit cell shown below is **JEE-2010**



- (A) 39.27% (B) 68.02% (C) 74.05% (D) 78.54%

13. **D**



Number of atoms per unit cell

$$= 4 \times \frac{1}{4} + 1 = 2$$

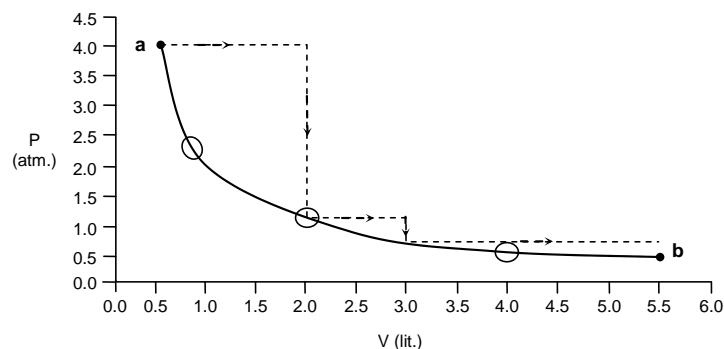
$$\sqrt{2} L = 4a. \Rightarrow a = \frac{L}{2\sqrt{2}}$$

$$\text{Packing fraction} = \frac{2 \times \pi \left( \frac{L}{2\sqrt{2}} \right)^2}{L^2}$$

$$= \frac{\pi}{8} = 0.7854$$

% efficiency = 78.54%.

14. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is  $w_s$  and that along the dotted line path is  $w_d$ , then the integer closest to the ratio  $w_d/w_s$  is **JEE-2010**



14 **2**

$$W_d = 4(2-0.5) + 1(3-2) + 0.5(5.5-3)$$

$$= 6 + 1 + 1.25 = 8.25 \text{ L-atm}$$

$$W_s = 2.303 nRT \log\left(\frac{V_2}{V_1}\right) \quad nRT = PV = 4 \times 0.5$$

$$= 2.303 \times 2 \times \log\left(\frac{5.5}{0.5}\right)$$

$$= 4.79 \text{ L-atm.}$$

$$\frac{W_d}{W_s} = \frac{8.25}{4.79} = 1.72 \approx 2.$$

15. Silver (atomic weight = 108 g mol<sup>-1</sup>) has a density of 10.5 g cm<sup>-3</sup>. The number of silver atoms on a surface of area 10<sup>-12</sup> m<sup>2</sup> can be expressed in scientific notation as  $y \times 10^x$ . The value of  $x$  is **JEE-2010**

15. **7**

'Ag' crystallizes in 'CCP' manner and  $n = 4$

$$d = \frac{n \times A}{N_0 \cdot a^3} \quad 10.5 = \frac{4 \times 108}{6 \times 10^{23} \times a^3}$$

$$a \approx 4 \times 10^{-8} \text{ cm}$$

$$\text{Volume of the solid given} = 10^{-12} \times 10^4 \times 4 \times 10^{-8} = 4 \times 10^{-16} \text{ cc.}$$

$$\text{Number of atoms per CC} = \frac{10.5}{108} \times 6 \times 10^{23} = 5.8 \times 10^{22}$$

$$\therefore \text{no of 'Ag' atom} = 4 \times 10^{-16} \times 5.8 \times 10^{22} = 2.74 \times 10^7$$

**Paragraph for questions 16 to 18**

The hydrogen-like species  $\text{Li}^{2+}$  is in a spherically symmetric state  $S_1$  with one radial node. Upon absorbing light the ion undergoes transition to a state  $S_2$ . The state  $S_2$  has one radial node and its energy is equal to the ground state energy of the hydrogen atom. **JEE-2010**

16. The state  $S_1$  is  
 (A) 1s (B) 2s (C) 2p (D) 3s
17. Energy of the state  $S_1$  in units of the hydrogen atom ground state energy is  
 (A) 0.75 (B) 1.50 (C) 2.25 (D) 4.50
18. The orbital angular momentum quantum number of the state  $S_2$  is  
 (A) 0 (B) 1 (C) 2 (D) 3

16.

**B**

No. of radial nodes = 1

$$\Rightarrow -1 = 1 - n$$

$$\Rightarrow n - \ell = 2$$

Orbital	$n - \ell$
1s	1
2s	2
2p	1
3s	3

17.

**C**

$$\begin{aligned} \text{Energy of state } S_1 &= \frac{E_1(\text{H})}{n^2} \times Z^2 \\ &= \frac{E_1(\text{H})}{4} \times 9 \\ &= 2.25 E_1(\text{H}) \end{aligned}$$

18.

**B**

Energy of state  $S_2 = E_1(\text{H})$

$$\Rightarrow \frac{E_1(\text{H})}{n^2} \times 9 = E_1(\text{H})$$

$$\Rightarrow n = 3$$

Now, no. of radial nodes = 1

$$\Rightarrow n - \ell - 1 = 1$$

$$\Rightarrow 2 - \ell = 1$$

$$\Rightarrow \ell = 1$$

19.

Given that the abundances of isotopes  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$  are 5%, 90% and 5%, respectively, the atomic mass of Fe is

**JEE-2009**

(A) 55.85

(B) 55.95

(C) 55.75

(D) 56.05

19.

**B**

**Sol:**

The abundance of  $^{54}\text{Fe} = 5\%$

$^{56}\text{Fe} = 90\%$

$^{57}\text{Fe} = 5\%$

$$\therefore \text{The atomic mass of Fe is} = \frac{5(54) + 90(56) + (57) \times 5}{100}$$

20.

The term that corrects for the attractive forces present in a real gas in the van der Waals equation is

**JEE-2009**

(A)  $nb$

(B)  $\frac{an^2}{V^2}$

(C)  $-\frac{an^2}{V^2}$

(D)  $-nb$

20.

**B**

21. Among the electrolytes  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NH}_4\text{Cl}$ , the most effective coagulating agent for  $\text{Sb}_2\text{S}_3$  sol is

**JEE-2009**

(A)  $\text{Na}_2\text{SO}_4$

(B)  $\text{CaCl}_2$

(C)  $\text{Al}_2(\text{SO}_4)_3$

(D)  $\text{NH}_4\text{Cl}$

21.

**C**

**Sol:**

$\text{Sb}_2\text{S}_3$  is an negatively charged sol, so among the given cations  $\text{Al}^{3+}$  has highest flocculating power.

22.

The Henry's law constant for the solubility of  $\text{N}_2$  gas in water at 298 K is  $1.0 \times 10^5$  atm. The mole fraction of  $\text{N}_2$  in air is 0.8. The number of moles of  $\text{N}_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is

**JEE-2009**

22. (A)  $4.0 \times 10^{-4}$  (B)  $4.0 \times 10^{-5}$  (C)  $5.0 \times 10^{-4}$  (D)  $4.0 \times 10^{-6}$   
**A**

**Sol :** Henry's law is  $P = K_H X$

$$n_{N_2} = n_{H_2O} \times \frac{P_{N_2}}{K_H^{N_2}}$$

Where  $n_{N_2}$  = no. of moles of nitrogen,  $N_2$  dissolved.

$$P_{N_2} = X_{N_2} P_{air}$$

$n_{H_2O}$  = no. of moles of solvent

$$= 0.8 \times 5$$

$P_{N_2}$  = partial pressure of gas dissolved.

$$P_{N_2} = 4 \text{ atm}$$

$K_H^{N_2}$  = Henry's law constant for gas dissolved

$$n_{N_2} = 10 \times \frac{4}{1 \times 10^5}$$

$X_{N_2}$  = mole fraction of Nitrogen,  $N_2$  in air

$$n_{N_2} = 4 \times 10^{-4} \text{ moles .}$$

23. The correct statement(s) regarding defects in solids is(are) **JEE-2009**  
 (A) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion  
 (B) Frenkel defect is a dislocation defect  
 (C) Trapping of an electron in the lattice leads to the formation of F-center  
 (D) Schottky defects have no effect on the physical properties of solids

23. **B, C**

24. Match each of the diatomic molecules in **Column I** with its property/properties in **Column II**.

**JEE-2009**

Column - I		Column - II	
(A)	$B_2$	(p)	Paramagnetic
(B)	$N_2$	(q)	Undergoes oxidation
(C)	$O_2^-$	(r)	Undergoes reduction
(D)	$O_2$	(s)	Bond order $\geq 2$
		(t)	Mixing of 's' and 'p' orbitals

24. **A** → p, q, r, t ; **B** → q, r, s, t; **C** → p, q, r ; **D** → p, q, r, s

25. For a first order reaction  $A \rightarrow P$ , the temperature (T) dependent rate constant (k) was found to follow the equation  $\log k = -(2000) \frac{1}{T} + 6.0$ . The pre-exponential factor A and the activation energy  $E_a$ ,

respectively, are **JEE-2009**

(A)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $9.2 \text{ kJ mol}^{-1}$

(B)  $6.0 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$

(C)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$

(D)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $38.3 \text{ kJ mol}^{-1}$

25. **D**

**Sol.**  $\log K = \log A - \frac{E_a}{2.303RT}$

$$\frac{E_a}{2.303R} = 2000$$

$$\log A = 6$$

26. The spin only magnetic moment value (in Bohr magneton units) of  $Cr(CO)_6$  is

**JEE-2009**

(A) 0

(B) 2.84

(C) 4.90

(D) 5.92

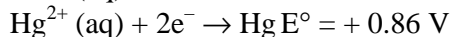
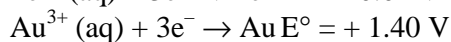
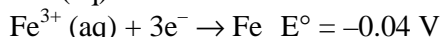
26. **A**

**Sol.** CO is strong field ligand

$\text{Cr}(\text{CO})_6$  : Cr is in zero oxidation state. All 6 electrons present in Cr will be paired. So no unpaired electrons

27. For the reduction of  $\text{NO}_3^-$  ion in an aqueous solution,  $E^\circ$  is + 0.96 V. Values of  $E^\circ$  for some metal ions are given below.

**JEE-2009**



The pair(s) of metals that is(are) oxidized by  $\text{NO}_3^-$  in aqueous solution is (are)

- (A) V and Hg      (B) Hg and Fe      (C) Fe and Au      (D) Fe and V

27. **A, B, D**

**Sol.**  $E^\circ_{\text{V}/\text{V}^{2+}} = +1.19 \text{ V}$

$$E^\circ_{\text{Fe}/\text{Fe}^{3+}} = +0.04 \text{ V}$$

$$E^\circ_{\text{Au}/\text{Au}^{3+}} = -1.4 \text{ V}$$

$$E^\circ_{\text{Hg}/\text{Hg}^{2+}} = -0.86 \text{ V}$$

The cell constructed with Au will have negative  $E^\circ$ . (+ 0.96 + (-1.4) = -0.44) with remaining three metals it will be positive.

28. Among the following, the state function(s) is (are)

**JEE-2009**

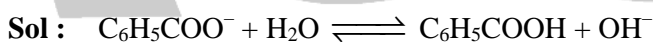
- (A) Internal energy      (B) Irreversible expansion work  
(C) Reversible expansion work      (D) Molar enthalpy

28. **A, D**

29. The dissociation constant of a substituted benzoic acid at  $25^\circ\text{C}$  is  $1.0 \times 10^{-4}$ . The pH of a 0.01 M solution of its sodium salt is

**JEE-2009**

29. **8**



Initial conc .	0.01	0	0
Eq. conc.	$0.01(1 - \infty)$	$0.01 \infty$	$0.01 \infty$

For conjugate acid – base pair,

$$K_w = K_a \times K_b$$

$$\Rightarrow K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

$$K_b = \frac{0.01 \infty \times 0.01 \infty}{0.01(1 - \infty)}$$

$$\Rightarrow 10^{-10} = 0.01 \infty$$

$$\Rightarrow \infty = \frac{10^{-10}}{0.01} = 10^{-8}$$

$$[\text{OH}^-] = 0.01 \infty = 10^{-6}$$

$$p^{\text{OH}} = 6$$

$$p^{\text{H}} = 8$$

30. At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is

**JEE-2009**

30. **4**

Sol :  $\sqrt{\frac{3RT_1}{40}} = \sqrt{\frac{2RT_2}{M_y}}$   
 $\Rightarrow \frac{3T_1}{40} = \frac{2T_2}{M_y}$   
 $\Rightarrow 30 = \frac{2 \times 60}{M_y}$   
 $\Rightarrow M_y = 4$   
 Mol. Wt. of gas y = 4.

31. The total number of  $\alpha$  and  $\beta$  particles emitted in the nuclear reaction  ${}_{92}^{238}\text{U} \rightarrow {}_{82}^{214}\text{Pb}$  is  
**JEE-2009**

31. 8

Sol :  ${}_{92}^{238}\text{U} \xrightarrow{x\alpha, y\beta} {}_{82}^{214}\text{Pb}$   
 $92 - 2x + y = 82$   
 $\Rightarrow 2x - y = 10 \quad \dots(1)$   
 $238 - 4x = 214 \quad \dots(2)$   
 $\Rightarrow 4x = 24$   
 $\therefore x = 6$   
 from equation (1),  
 $y = 2$   
 Total. No of  $\alpha$  &  $\beta$  particles =  $6 + 2 = 8$

32. The coordination number of Al in the crystalline state of  $\text{AlCl}_3$  is . **JEE-2009**

32. 6

Sol : The crystalline solid has a layer lattice with six co-ordination  $\text{Al}$ .  
 Coordination No. of  $\text{Al} = 6$ .

33. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is  $2.5 \text{ kJ K}^{-1}$ , the numerical value for the enthalpy of combustion of the gas in  $\text{kJ mol}^{-1}$  is **JEE-2009**

33. 9

Sol :  $q = \text{Heat capacity} \times \Delta T$   
 $= 2.5 \times 0.45$   
 $= 1.125 / \text{g}$   
 for 1 mole,  $q = 1.125 \times \frac{28}{3.5} = 9$   
 Heat of combustion =  $-9 \text{ kJ mol}^{-1}$

34. Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio  $\left(\frac{k_1}{k_0}\right)$  of the rate constants for first order ( $k_1$ ) and zero order ( $k_0$ ) of the reactions is

**JEE-2008**

- (A)  $0.5 \text{ mol}^{-1} \text{ dm}^3$  (B)  $1.0 \text{ mol dm}^{-3}$  (C)  $1.5 \text{ mol dm}^{-3}$  (D) 2.0

34. (A)



$$K_1 = \frac{0.693}{t_{\frac{1}{2}}} \quad K_0 = \frac{a}{2t_{0.1}^{\frac{1}{2}}}, \quad \frac{K_1}{K_0} = \frac{0.693}{t_{\frac{1}{2}}} \times \frac{2t_{0.1}^{\frac{1}{2}}}{a}$$

or,  $\frac{K_1}{K_0} = \frac{0.693}{40} \times \frac{40}{1.386}$  or,  $\frac{K_1}{K_0} = \frac{0.693}{1.386} = 0.5 \text{ mol}^{-1} \text{ dm}^3$

35. 2.5 mL of  $\frac{2}{5} \text{M}$  weak monoacidic base ( $K_b = 1 \times 10^{-12}$  at  $25^\circ\text{C}$ ) is titrated with  $\frac{2}{15} \text{M}$  HCl in water at  $25^\circ\text{C}$ . The concentration of  $\text{H}^+$  at equivalence point is ( $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ ) **JEE-2008**  
 (A)  $3.7 \times 10^{-13} \text{ M}$  (B)  $3.2 \times 10^{-7} \text{ M}$  (C)  $3.2 \times 10^{-2} \text{ M}$  (D)  $2.7 \times 10^{-2} \text{ M}$
35. (C)

$$M_1 V_1 = M_2 V_2$$

$$\frac{2}{5} \times 2.5 = \frac{2}{15} V_{\text{HCl}}$$

$$\Rightarrow V_{\text{HCl}} = 7.5 \text{ ml}$$

Meq of base = 1

$$[\text{Base}] = \frac{1}{10} \text{M}$$

$$[\text{H}^+] = \sqrt{\frac{K_w}{K_b} \times C}$$

$$[\text{H}^+] = \sqrt{\frac{10^{-14}}{10^{-12}} \times 0.1}$$

$$\Rightarrow [\text{H}^+] = 3.2 \times 10^{-2} \text{M}$$

36. A gas described by van der Waals equation **JEE-2008**  
 (A) behaves similar to an ideal gas in the limit of large molar volumes  
 (B) behaves similar to an ideal gas in the limit of large large pressures  
 (C) is characterized by van der Waals coefficients that are dependent on the identify of the gas but are independent of the temperature  
 (D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

- 36 (A), (C) and (D)

$$\bullet \left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

If  $V_m$  is large

$$PV_m = RT$$

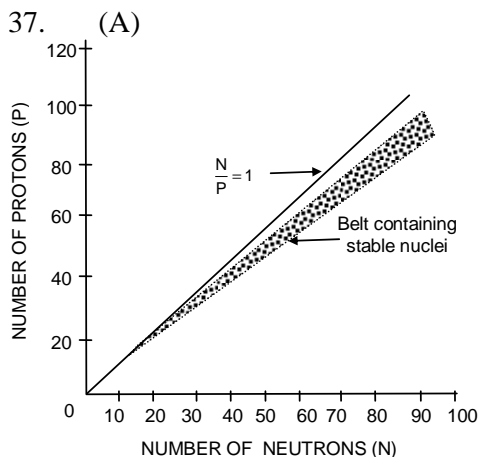
- 'a' and 'b' are characteristics of vanderwaal's gas and independent of temperature.
- Due to attractive forces among the gaseous molecules, the pressure exerted is lower than the pressure exerted by the ideal gas.

37. STATEMENT – 1: The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of  $45^\circ$  slope as the atomic number is increased. **JEE-2008**

and

STATEMENT – 2: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

- (A) Statement–1 is True, Statement–2 is True; Statement–2 is a correct explanation for Statement–1  
 (B) Statement–1 is True, Statement–2 is True; Statement–2 is **NOT** a correct Explanation for Statement–1  
 (C) Statement–1 is True, Statement–2 is False  
 (D) Statement–1 is False, Statement–2 is True



38. STATEMENT – 1: For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero. **JEE-2008**

and

STATEMENT – 2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

- (A) Statement–1 is True, Statement–2 is True; Statement–2 is a correct explanation for Statement–1  
 (B) Statement–1 is True, Statement–2 is True; Statement–2 is **NOT** a correct Explanation for Statement–1  
 (C) Statement–1 is True, Statement–2 is False  
 (D) Statement–1 is False, Statement–2 is True
38. (D)  $\Delta G = \Delta G^0 + RT \ln Q$   
 At equilibrium,  $\Delta G = 0$  ( $\Delta G^0 \neq 0$ )  
 $\Delta G^0 = -RT \ln K$   
 If  $\Delta G$  is – ve, reaction will be spontaneous.

### Paragraph for Question Nos. 39 to41

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogenous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles. **JEE-2008**

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water ( $K_f^{\text{water}}$ ) = 1.86 K kg mol<sup>-1</sup>

Freezing point depression constant of ethanol ( $K_f^{\text{ethanol}}$ ) = 2.0 K kg mol<sup>-1</sup>

Boiling point elevation constant of water ( $K_b^{\text{water}}$ ) = 0.52 K kg mol<sup>-1</sup>

Boiling point elevation constant of ethanol ( $K_b^{\text{ethanol}}$ ) = 1.2 K kg mol<sup>-1</sup>

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol<sup>-1</sup>

Molecular weight of ethanol = 46 g mol<sup>-1</sup>

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

39. The freezing point of the solution **M** is  
 (A) 268.7 K (B) 268.5 K (C) 234.2 K (D) 150.9 K

39. (D)

$$\text{Molality of the solution } m = \frac{0.1 \times 1000}{0.9 \times 46} = 2.4$$

$$\Delta T_f = K_f \times m = 2 \times 2.4 = 4.8$$

$$T_f = 155.7 - 4.8 = 150.9 \text{ K}$$

40. The vapour pressure of the solution **M** is  
 (A) 39.3 mm Hg (B) 36.0 mm Hg (C) 29.5 mm Hg (D) 28.8 mm Hg

40. (B)  
 $P = x_A p_A^0 = (0.9 \times 40) = 36 \text{ mm of Hg}$

41. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is  
 (A) 380.4 K (B) 376.2 K (C) 375.5 K (D) 354.7 K

41. (B)  
 Molality of the solution in which mole fraction of H<sub>2</sub>O 0.9, is,

$$m = \frac{0.1}{0.9 \times 18} \times 1000 = 6.17 \text{ m}$$

$$\begin{aligned} \Delta T_b &= K_b \times m \\ &= 0.52 \times 6.17 \\ &= 3.2 \end{aligned}$$

$$\therefore T_b = 373 + 3.2 = 376.2 \text{ K}$$

42. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H<sub>2</sub> gas at the cathode is (1 Faraday = 96500 C mol<sup>-1</sup>)

**JEE-2008**

- (A) 9.65 x 10<sup>4</sup> (B) 19.3 x 10<sup>4</sup> sec (C) 28.95 x 10<sup>4</sup> sec (D) 38.6 x 10<sup>4</sup> sec

42. (B)  
 0.01 mole of H<sub>2</sub> = 0.02 equivalents of H<sub>2</sub> ≡ 0.02 F

$$\begin{aligned} i &= \frac{Q}{t} \\ \Rightarrow 10 \times 10^{-3} &= \frac{0.02 \times 96,500}{t} \\ \Rightarrow t &= \frac{0.02 \times 96,500}{10^{-2}} \\ \Rightarrow t &= 19.3 \times 10^4 \text{ sec} \end{aligned}$$

43. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is

**JEE-2008**

- (A) CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Br<sup>-</sup> (B) CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub><sup>-</sup>Na<sup>+</sup>  
 (C) CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>COO<sup>-</sup>Na<sup>+</sup> (D) CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>Br<sup>-</sup>

43. (B)  
 Detergents have more tendency to form micelles. Due to higher molar mass and greater polarity, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub><sup>-</sup>Na<sup>+</sup> will form micelles at lowest molar concentration.

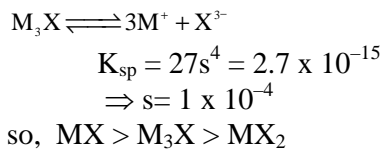
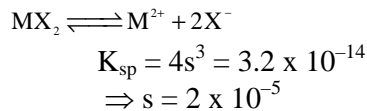
44. Solubility product constants (K<sub>sp</sub>) of salts of types MX, MX<sub>2</sub> and M<sub>3</sub>X at temperature "T" are 4.0 x 10<sup>-8</sup>, 3.2 x 10<sup>-14</sup> and 2.7 x 10<sup>-15</sup> respectively. Solubilities (mol dm<sup>-3</sup>) of the salts at temperature "T" are in the order

**JEE-2008**

- (A) MX > MX<sub>2</sub> > M<sub>3</sub>X (B) M<sub>3</sub>X > MX<sub>2</sub> > MX  
 (C) MX<sub>2</sub> > M<sub>3</sub>X > MX (D) MX > M<sub>3</sub>X > MX<sub>2</sub>

44. (D)  

$$\begin{aligned} \text{MX} &\rightleftharpoons \text{M}^+ + \text{X}^- \\ \text{K}_{\text{sp}} &= s^2 = 4 \times 10^{-8} \\ \Rightarrow s &= 2 \times 10^{-4} \end{aligned}$$



45. STATEMENT-1 : **JEE-2008**  
 There is a natural asymmetry between converting work to heat and converting heat to work.  
**and**  
 STATEMENT-2 :  
 No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.  
 (A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1  
 (B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is **NOT** a correct explanation for STATEMENT-1  
 (C) STATEMENT-1 is True, STATEMENT-2 is False  
 (D) STATEMENT-1 is False, STATEMENT-2 is True
45. (A)

**Paragraph for Question Nos. 46 to 48**

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'. **JEE-2008**

46. The number of atoms in this HCP unit cell is  
 (A) 4 (B) 6 (C) 12 (D) 17
46. (B)  
 Effective number of atoms per unit cell of HCP = 6
47. The volume of this HCP unit cell is  
 (A)  $24\sqrt{2}r^3$  (B)  $16\sqrt{2}r^3$  (C)  $12\sqrt{2}r^3$  (D)  $\frac{64}{3\sqrt{3}}r^3$
47. (A)  
 The volume of HCP unit cell =  $24\sqrt{2} r^3$
48. The empty space in this HCP unit cell is  
 (A) 74% (B) 47.6% (C) 32% (D) 26%
48. (D)  
 % packing fraction = 74%  
 % of empty space = 26%.

49. Match the entries in **Column I** with the correctly related quantum number(s) in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 x 4 matrix given in the ORS.

Column I	Column II
(A) Orbital angular momentum of the electron in a hydrogen-like atomic orbital	<b>JEE-2008</b> (p) Principal quantum number
(B) A hydrogen-like one-electron wave function obeying Pauli principle	(q) Azimuthal quantum number
(C) Shape, size and orientation of hydrogen-like atomic orbitals	(r) Magnetic quantum number
(D) Probability density of electron at the nucleus in hydrogen-like atom	(s) Electron spin quantum number

49. (A) - q  
(B) - p, q, r  
(C) - p, q, r  
(D) - p, q, r

50. When 20g of naphthoic acid ( $C_{11}H_8O_2$ ) is dissolved in 50g of benzene ( $K_f = 1.72 \text{ K kg mol}^{-1}$ ), a freezing point depression of 2K is observed. The van't Hoff factor ( $i$ ) is **JEE-2008**

- (A) 0.5 (B) 1  
(C) 2 (D) 3

50. (A)  
 $\Delta T_f = i K_f m$   
 $2 = i \times 1.72 \times \frac{20}{172} \times \frac{1000}{50}$   
 $\therefore i = 0.5$

51. The value of  $\log_{10}K$  for a reaction  $A \rightleftharpoons B$  is **JEE-2008**

(Given:  $\Delta_r H_{298K}^\circ = -54.07 \text{ kJ mol}^{-1}$ ,  $\Delta_r S_{298K}^\circ = 10 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $2.303 \times 8.314 \times 298 = 5705$ )

- (A) 5 (B) 10 (C) 95 (D) 100

51. (B)  
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -2.303 RT \log_{10} K$   
 or,  $-54.07 - 298 \times \frac{10}{1000} = -\frac{5705}{1000} \log_{10} K$   
 $\therefore \log_{10} K = 10$

52. The species having bond order different from that in CO is **JEE-2008**

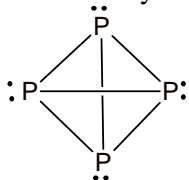
- (A)  $NO^-$  (B)  $NO^+$   
(C)  $CN^-$  (D)  $N_2$

52. (A)  
 Except  $NO^-$ , all other species have 14 electrons as there are in CO, so they have same bond order of 3.  
 $NO^-$  has 16  $e^-$ s and has a bond order of 2

53. The percentage of p-character in the orbitals forming P-P bonds in  $P_4$  is **JEE-2008**

- (A) 25 (B) 33  
(C) 50 (D) 75

53. (D)  
Since the hybridisation of P in  $P_4$  is  $sp^3$ , the % p-character is 75



54. STATEMENT-1: Micelles are formed by surfactant molecules above the critical micellar concentration CMC. **JEE-2008**  
**because**  
STATEMENT-2: The conductivity of a solution having surfactant molecules decreases sharply at the CMC.  
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1  
(B) Statement-1 is True, Statement-2 is True; Statement-2 is **NOT** a correct explanation for statement-1  
(C) Statement-1 is True, Statement-2 is False  
(D) Statement-1 is False, Statement-2 is True
55. (B)  
No. of ions per unit volume decreases due to aggregation of ions at CMC, hence conductivity decreases.

**Paragraph for Question Nos. 56 to 58**

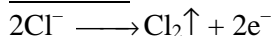
Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately  $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept. **JEE-2008**

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass: Na = 23, Hg = 200; 1 Faraday = 96500 coulombs).

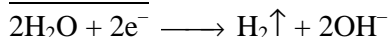
56. The total number of moles of chlorine gas evolved is  
(A) 0.5 (B) 1.0  
(C) 2.0 (D) 3.0

56. (B)

At anode:



At cathode:



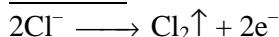
The solution contains 2 moles of  $Cl^-$  ions, which on electrolysis produce 1 mole of  $Cl_2$  gas.

57. If the cathode is a Hg electrode, the maximum weight(g) of amalgam formed from this solution is  
(A) 200 (B) 225  
(C) 400 (D) 446

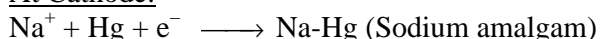
57. (D)

If Hg is used as cathode then following reactions occur

At anode:



At Cathode:



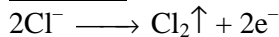
Since 2 moles of  $Na^+$  ions are there in solution, 2 moles of sodium amalgam will be formed.

∴ weight of amalgam = 223 x 2 = 446 g

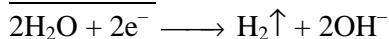
58. The total charge (coulombs) required for complete electrolysis is  
 (A) 24125 (B) 48250  
 (C) 96500 (D) 193000

58. (D)

At anode:



At Cathode:



2 moles of e<sup>-</sup>s are involved in electrolysis

∴ total charge required = 96500 x 2 = 193000 Coulombs.

59. Match gases under specified conditions listed in **Column I** with their properties / laws in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 x 4 matrix given in the ORS.

**JEE-2008**

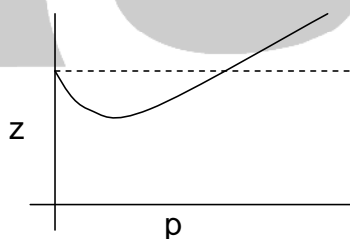
Column I		Column II	
(A)	hydrogen gas (P = 200 atm, T = 273 K)	(p)	compressibility factor ≠ 1
(B)	hydrogen gas (P ≈ 0 atm, T = 273 K)	(q)	attractive forces are dominant
(C)	CO <sub>2</sub> (P = 1 atm, T = 273 K)	(r)	PV = nRT
(D)	real gas with very large molar volume	(s)	P(V - nb) = nRT

59. A- p, s ; B- r ; C- p, q ; D- p, s

(A) H<sub>2</sub> is the lightest gas and has very weak attractive forces, hence 'a' is negligible. It always shows positive deviation.

(B) H<sub>2</sub> at very low pressure i.e. p ≈ 0, shows ideal behaviour i.e. PV = nRT

(C) For CO<sub>2</sub>, the following graph is valid



At low pressure,  $z < 1$  & at high pressure,  $z > 1$ .  
 According to conditions given at very low temperature, attractive forces are dominant.

(D)  $\left(P + \frac{a}{v^2}\right)(v - b) = RT$

at large molar volume

$v - b \neq v$ ; but  $\left(P + \frac{a}{v^2}\right) \approx P$

hence, the above Vanderwaal's equation becomes  $P(v - b) = RT$  & hence  $z \neq 1$