Advanced Problem Package	Stoichiometry-I & II

SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. In the reaction : $CrO_5 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + H_2O + O_2$
How many moles of O_2 are liberated by 1 mol of CrO_5 in above reaction?
(A) 5/2 **(B)** 5/4 **(C)** 9/2 **(D)** 7/4

2. A mixture of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ required equal volumes of 0.2 M $KMnO_4$ and 0.2 M NaOH separately for complete titration. The mole ratio of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ in the mixture is :
(A) 2/11 **(B)** 11/2 **(C)** 5/2 **(D)** 7/2

3. Following are given some of the unbalanced redox reactions showing all chemical speices participating during the reactions. Identify the redox reaction in which whole of reducing agent has not converted to one product?

(A) $Au + KCN + H_2O + O_2 \longrightarrow K[Au(CN)_4] + KOH$

(B) $V(OH)_4Cl + FeCl_2 + HCl \longrightarrow VOCl_2 + H_2O + FeCl_3$

(C) $KMnO_4 + KOH \longrightarrow K_2MnO_4 + O_2 + H_2O$

(D) $MnO + PbO_2 + HNO_3 \longrightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$

4. A fluoride of Xenon reacts with excess of hydrogen to give 22.4 ml of Xenon at STP and liberated certain amount of HF, which is trapped in water. This hydrofluoric acid solution requires 60 ml of 0.1 M NaOH to neutralize it completely. The formula of Xenon fluoride will be:
(A) XeF_2 **(B)** XeF_4 **(C)** XeF_6 **(D)** XeF_8

5. 150 mL of solution of I_2 is divided into two unequal parts. 1st part reacts with 15 mL of 0.4 M Hypo solution in acidic medium. 2nd part was added to 100 mL of 0.3 M NaOH solution and residual base required 10 mL of 0.3 M H_2SO_4 solution for complete neutralization. What was the initial concentration of I_2?
(A) 0.08 M **(B)** 0.1 M **(C)** 0.2 M **(D)** 0.3 M

6. A sample of HCN yields potassium cyanide when titrated with 100 ml of 1 M KOH. The same HCN sample when titrated against 5 M $KMnO_4$ solution in acidic medium, the products formed are Mn^{2+}, NO_3^- and CO_2. The volume of $KMnO_4$ required would be:
(A) 400 ml **(B)** 120 ml **(C)** 200 ml **(D)** 40 ml

7. 1 mol of MnO_4^{2-} in alkaline aqueous medium disproportionates to :

(A) $\frac{2}{3}$ mol of MnO_4^- and $\frac{1}{3}$ mol of MnO_2 **(B)** $\frac{1}{3}$ mol of MnO_4^- and $\frac{2}{3}$ mol of MnO_2

(C) $\frac{1}{3}$ mol of Mn_2O_7 and $\frac{2}{3}$ mol of MnO_2 **(D)** $\frac{2}{3}$ mol of Mn_2O_7 and $\frac{1}{3}$ mol of MnO_2

8. RH_2 (ion exchange resin) can replace Ca^{2+} in hard water in a following way: $RH_2 + Ca^{2+} \longrightarrow RCa + 2H^{\oplus}$.

1 L of hard water after passing through RH_2 has pH = 2. Hence, hardness in ppm of Ca^{2+} is :

(A) 200 **(B)** 100 **(C)** 50 **(D)** 125

Paragraph for Questions 9 - 10

Air sample from an industrial area of Delhi, which is heavily polluted by CO_2, was collected and analysed. One such sample of 224 L of air measured at STP was passed through 500 mL of 0.1 M KOH solution, where CO_2(g) was absorbed completely. 50 mL of the above solution was then treated with excess of $BaCl_2$ solution where all the carbonate was precipitated as $BaCO_3$(s). The solution was filtered off and the filtrate required 30 mL of 0.1 M HCl solution for neutralisation.

9. The ppm strength of CO_2 (g) volume by volume (mL of CO_2 per 10^6 mL of air) is

(A) 224 **(B)** 2240 **(C)** 100 **(D)** 1000

10. The weight of the precipitate of $BaCO_3$(s) obtained from 50 mL of the above test solution is:
(Ba = 137, C = 12, O = 16, Mw($BaCO_3$) = 197g mol^{-1})

(A) 3.94 g **(B)** 0.394 g **(C)** 0.197 g **(D)** 1. 97 g

Paragraph for Questions 11 - 13

100 mL solution of ferric alum [$Fe_2(SO_4)_3.(NH_4)_2.SO_4.\ 24H_2O$](Mw = 964 g/$mol^{-1}$) containing 2.41g of salt was boiled with Fe when following reaction took place:

$Fe + Fe_2(SO_4)_3 \rightarrow 3\ FeSO_4$.

The unreacted iron was filtered off and the solution was titrated with M/60 $K_2Cr_2O_7$ solution in acidic medium.

11. Number of moles of $FeSO_4$ formed when Fe reacts with $Fe_2(SO_4)_3$ is :

(A) 0.0075 **(B)** 0.005 **(C)** 0.001 **(D)** 0.002

12. If instead of Fe, plate of Cu is put in $Fe_2(SO_4)_3$ then number of moles of $FeSO_4$ formed will be:

(A) 0.0075 **(B)** 0.005 **(C)** 0.001 **(D)** 0.002

13. Volume of $K_2Cr_2O_7$ reacted with $FeSO_4$ is:

(A) 25 mL **(B)** 50 mL **(C)** 75 mL **(D)** 100 mL

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

14. A solution containing Cu^{2+} and $C_2O_4^{2-}$ ions is titrated with 20 mL of M/4 $KMnO_4$ solution in acidic medium. The resulting solution is treated with excess of KI after neutralisation. The evolved I_2 is then absorbed is 25 mL of M/10 hypo solution.Which of the following statement(s) is/are correct?

(A) The difference in the number of mmol of Cu^{2+} and $C_2O_4^{2-}$ ions in the solution is 10 mmol

(B) The difference in the number of mmol of Cu^{2+} and $C_2O_4^{2-}$ ions in the solution is 12.5 mmol

(C) The equivalent weight of Cu^{2+} salt in the titration with KI is equal to the atomic weight of Cu^{2+}salt itself

(D) n_f of KI during reaction with Cu^{2+} salt is 1

15. 100 mL of M/10 $Ca(MnO_4)_2$ in acidic medium can be reduced completely with :

(A) 100 mL of 1 M $FeSO_4$ solution. **(B)** $\frac{100}{3}$ mL of 1 M FeC_2O_4 solution.

(C) 16.6 mL of 1 M $K_2Cr_2O_7$ solution. **(D)** 50 mL of 1 M $C_2O_4^{2-}$ solution.

16. Equivalent weight of Na_2HPO_4 can be :

(A) M/2 as base if H^+ is taken in excess.

(B) M/1 as acid if OH^- is taken in excess

(C) M/1 as base if reacted with 1 equivalent of H^+

(D) Defined only as a base and not as an acid for this salt

17. (*x*) g of H_2O_2 requires 100 mL of M/5 $KMnO_4$ in a titration having pOH =1. Which of following statement(s) is(are) correct?

(A) The value of *x* is 1.7 g.

(B) The value of *x* is 0.34 g.

(C) $MnO_4^{\ominus}$ changes to MnO_4^{2-}

(D) H_2O_2 changes to O_2.

18. 20 mL of 6 M HCl is mixed with 50 mL of 2 M $Ba(OH)_2$ and 30 mL of water is added. Select the correct statement(s):

(A) $[OH^-]_{mix} = 0.8$ M

(B) $[Cl^-]_{mix} = 1.2$ M

(C) $[Ba^{2+}]_{mix} = 0.2$ M

(D) 40 mmol of OH^- are in excess.

19. A sample of oleum is labelled as 112% . Which of the following statement(s) is(are) correct for this sample?

(A) Addition of 9 g of water will leave 1/6 mole of SO_3 unreacted in it

(B) Addition of 9 g of water will make total mass of H_2SO_4 as 95.7 grams

(C) 53.3 g of H_2SO_4 is present in sample and rest is unreacted SO_3

(D) Addition of 12 g of water would react with 53.3 g of unreacted SO_3

20. The hardness of water due to HCO_3^- is 122 ppm. Select the correct statement(s).

(A) The hardness of water in terms of $CaCO_3$ is 200 ppm.

(B) The hardness of water in terms of $CaCO_3$ is 100 ppm.

(C) The hardness of water in terms of $CaCl_2$ is 222 ppm.

(D) The hardness of water in terms of $MgCl_2$ is 95 ppm.

21. One mole of Fe_2S_3 , 2 moles of H_2O and 3 moles of O_2 are allowed to react in following way :

$$2Fe_2S_3(s) + 6H_2O(l) + 3O_2(g) \longrightarrow 4Fe(OH)_3(s) + 6S(s)$$

Select the corect statement(s).

(A) H_2O would act as limiting reagent.

(B) 1.33 moles of $Fe(OH)_3$ is formed.

(C) 6 moles of S is formed.

(D) It is a non redox reaction.

22. Half litre each of three samples of H_2O_2 labelled as 10 volume , 15 volume , 20 volume are mixed and then solution is made 3 litre by addition of water. Select the correct statement(s).

(A) Final H_2O_2 solution would be labelled as 7.5 volume

(B) Normality of final H_2O_2 solution is 1.34

(C) Normality of final H_2O_2 solution is 1.5

(D) Final H_2O_2 solution would be labelled as 6.5 volume

23. Consider the following redox reaction : $KMnO_4 + Na_2S_2O_3 + H^+ \longrightarrow Mn^{2+} + SO_4^{2-} + K^+$

Which of the following is(are) true regarding the above reaction ?

(A) $\frac{5}{8}$ mol of $Na_2S_2O_3$ is oxidised by 1 mole of $KMnO_4$

(B) Oxidation number of sulphur changes from $+4$ to $+12$

(C) Change of medium from acidic to basic will have no effect on the stoichiometry of reaction

(D) Change in medium from acidic to basic will change the nature of product

24. Which of the following can be oxidised further with a strong oxidising agent ?

(A) SO_2 **(B)** MnO_2 **(C)** Al_2O_3 **(D)** CrO_3

25. A_2O_n is oxidised to AO_3^- by $KMnO_4$ solution in acidic medium. If 1.34 mmol of A_2O_n requires 32.2 mL of 0.05 M acidified $KMnO_4$ solution for complete oxidation, which of the following statement(s) is (are) correct ?

(A) The value of $n = 2$

(B) Empirical formula of oxide of AO

(C) 1 mol of A_2O_n would require 1 mol of acidified $K_2Cr_2O_7$ solution

(D) 'A' can be metal belonging to Group-II of Periodic Table

26. 1.25 g of an acid is completely neutralised by 25 mL of a 0.25 M $Ba(OH)_2$ solution. Which of the following statement(s) is (are) correct ?

(A) If the acid is dibasic, its molar mass would be 200

(B) If the acid is monobasic, its molar mass would be 400

(C) 0.50 g of the same acid would neutralize completely 12.5 mL of a 0.40 M NaOH solution

(D) 1g of the same acid would neutralize completely 25 mL of a 0.40 M $Ca(OH)_2$ solution

27. 5 mmol of SO_2Cl_2 is hydrolysed completely to make a 100 mL solution. Which of the following statements is(are) correct ? (Assume no gases were allowed to escape out of solution)

(A) The solution would be 0.05 M in H_2SO_4

(B) The solution would be 0.05 M in HCl

(C) If 10 mL of the stock solution is neutralised by 0.2 M NaOH, 10 mL of this base solution would be required

(D) If 10 mL of the solution is titrated with excess of $AgNO_3$, 1.5 mmol of AgCl would be formed

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labeled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

28. Given two mixtures: (A) NaOH and Na_2CO_3 (B) and $NaHCO_3$ and Na_2CO_3.

100 mL of mixture (A) required ‘a’ and ‘b’mL of 1M HCl in separate titration using phenolphthalein and methyl orange indicators while 100 mL of mixture' (B) required ‘x’ and ‘y’ mL of same HCl solution is separate titration using the same indicators.

	Column 1 [Mixture component]		**Column 2** [Milli moles]
(P)	Na_2CO_3 in mixture (A)	**1.**	(2a - b)
(Q)	Na_2CO_3 in mixture (B)	**2.**	(y–2x)
(R)	NaOH in mixture (A)	**3.**	x
(S)	$NaHCO_3$ in mixture (B)	**4.**	(b – a)

Codes :

	P	Q	R	S		P	Q	R	S
(A)	2	3	4	1	**(B)**	1	3	2	4
(C)	4	3	1	2	**(D)**	2	1	3	4

29. MATCH THE FOLLOWING :

	Column 1 [Reaction]		**Column 2** [The value of x]
(P)	2.5 mol each of ferric oxalate and ferrous oxalate mixture will require x **mol** of $KMnO_4$ in acidic medium for complete oxidation.	**1.**	11.0
(Q)	2.5 mol each of ferric oxalate and ferrous oxalate mixture will require x **mol** of $K_2Cr_2O_7$ in acidic medium for complete oxidation.	**2.**	7.0
(R)	2.5 mol each of CuS and Cu_2S mixture will require x **mol** of $KMnO_4$ in acidic medium for complete oxidation.	**3.**	4.5
(S)	2 mol each of $KMnO_4$ and $K_2Cr_2O_7$ mixture will require x **mol** of H_2O_2 in acidic medium for complete reduction.	**4.**	3.75

Codes :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	2	3	4	1	**(B)**	3	4	2	1
(C)	4	2	1	3	**(D)**	3	1	2	4

30. MATCH THE FOLLOWING :

	Column 1 [Redox Reaction]		**Column 2** [Molar ratio of reducing agent to oxidising agent]
(P)	$Cr_2O_7^{2-} + FeC_2O_4 \rightarrow Cr^{3+} + CO_2 + Fe^{3+}$	**1.**	3 : 2
(Q)	$H_2O_2 + Cr(OH)_3 \rightarrow CrO_4^{2-} + H_2O$	**2.**	2 : 1
(R)	$N_2H_4 + Cu(OH)_2 \rightarrow N_2O + Cu$	**3.**	1 : 3
(S)	$MnO_4^{\ominus} + C_2O_4^{2-} \longrightarrow MnO_2 + CO_2$	**4.**	2 : 3

Codes :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	2	3	4	1	**(B)**	1	3	2	4
(C)	2	4	3	1	**(D)**	4	1	3	2

31. **MATCH THE FOLLOWING :**

	Column 1		**Column 2** [Moles of product formed]
(P)	$N_2(g) + H_2(g) \rightarrow NH_3(g)$; (% yield = 80) 5 mol 9 mol ?	**1.**	3.5 mol
(Q)	$C(s) + H_2(g) \rightarrow C_2H_2(g)$; (% yield = 70) 12 mol 5 mol ?	**2.**	4 mol
(R)	$P_4(s) + O_2(g) \rightarrow P_2O_5(s)$; (% yield = 50) 5mol 20mol ?	**3.**	4.8 mol
(S)	$SO_2(g) + O_2(g) \rightarrow SO_3(g)$; (% yield = 75) 4 mol 3 mol ?	**4.**	3 mol

Codes :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	3	1	4	2	**(B)**	4	1	2	3
(C)	1	3	4	2	**(D)**	3	1	2	4

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

32. Number of moles of HCl used as reducing agent in the following reaction for per mole of $KMnO_4$ used is_________

$$KMnO_4 + HCl \longrightarrow KCl + MnCl_2 + Cl_2 + H_2O$$

33. 0.58 g of $CH_3(CH_2)_n$ COOH was burnt in excess of air and resulting gases (CO_2 and H_2O) were passed through excess NaOH. Then resulting solution was divided in two equal parts.

One part required 50 mL of 1.0 M HCl for complete neutralisation using phenolpthalein as indicator whereas another part required 80 ml of same HCl using methyl orange. Find the value of n.

34. $KIO_3 + KI + HCl \rightarrow KCl + I_2 + H_2O$
In the above reaction, if 1 mole of KIO_3 produces 0.27 mole of I_2, then what is percentage yield of reaction?

35. Moles of HNO_3 required as reducing agent to oxidise two moles of Mg in the following reaction is(are)_________

$$Mg + HNO_3 \longrightarrow Mg(NO_3) + N_2O + H_2O$$

36. A mixture is 0.04 M in Sn^{2+} and $x\,M$ in Fe^{2+}. 15.0 mL of this mixture required 18.0 mL of $0.125\,M\ Cr_2O_7^{2-}$ solution to oxidise to Sn^{4+} and Fe^{3+} in acidic medium, $Sn^{2+} + Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + Sn^{4+} + Fe^{3+}$. Thus, x is :

37. Amount of Mohr's salt $(FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O)$ having molar mass $392.0\,g\,mol^{-1}$ that must be dissolved in 250 mL solution to prepare an aqueous solution of density $1.00\,g\,mL^{-1}$ to have Fe^{2+} ion concentration 1 ppm by weight is $x \times 10^{-3}\,g$. Find the numerical value of x.

38. RH_2 is an ion exchange resin used to purify water in RO. It can replace Ca^{2+} in hard water.

$$RH_2 + Ca^{2+} \longrightarrow RCa + 2H^+$$

Water coming out of ion exchange resin has $[H^+] = 0.01M$. The, hardness of water in ppm of Ca^{2+} ion is ________.

39. In the Solvay process for producing sodium carbonate (Na_2CO_3), the following reactions occurs in sequence.

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

How much of Na_2CO_3 (in kg) would be produced per kg of NH_3 used if the process were 100% efficient ?

40. In one reaction with a 95% yield, 225 mL of 1.50 M $Na_2CO_3(aq)$, 22.1 g NO and a large excess O_2 are allowed to react $2Na_2CO_3(aq) + 4NO(g) + O_2(g) \longrightarrow 4NaNO_2(aq) + 2CO_2(g)$

What mass of $NaNO_2$ (in g) is obtained based on experimental yield ?

41. A solution contains 6.0 micromoles of Na_2SO_4 in 250 mL solution. Assuming no change in volume on dissolution, Na^+ in ppm present in solution is ________.

Advanced Problem Package	Atomic Structure

SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. The Schrodinger wave equation for hydrogen atom is : $\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/a_0}$

Where a_0 is Bohr's radius. If the radial node in 2s be at r_0, then r_0 would be equal to :

(A) $\frac{a_0}{2}$ **(B)** $2a_0$ **(C)** $\sqrt{2}a_0$ **(D)** $\frac{a_0}{\sqrt{2}}$

2. A hydrogen like species (atomic number *Z*) is present in a higher excited state of quantum number n. This excited atom can make a transition to the first excited state by successive emission of two photons of energies 10.20 eV and 17.0 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successive emission of two photons of energy 4.25 eV and 5.95 eV respectively. Determine the value of *Z*.

(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

3. The frequency of first line of Balmer series in hydrogen atom is ν_0. The frequency of corresponding line emitted by singly ionized helium atom is :

(A) $2\nu_0$ **(B)** $4\nu_0$ **(C)** $\nu_0 / 2$ **(D)** $\nu_0 / 4$

4. The angular momentum of an electron in a Bohr's orbit of H-atom is 3.1652×10^{-34} kg-m^2/sec. Calculate the wavenumber in terms of Rydberg constant (R) of the spectral line emitted when an electron falls from this level to the ground state.[Use h = 6.6×10^{-34} Js]

(A) $R\left(\frac{8}{9}\right)$ **(B)** $R\left(\frac{5}{9}\right)$ **(C)** $R\left(\frac{7}{9}\right)$ **(D)** None of these

5. Electron present in H atom jumps from energy level 3 to 1. Emitted photons when passed through a sample containing excited He^+ ion causes further excitation to some higher energy level. Determine principal quantum number of initial excited level & higher energy level of He^+. (Given $E_n = -13.6\frac{Z^2}{n^2}$) :

(A) $n_1 = 2,\ n_2 = 6$ **(B)** $n_1 = 2,\ n_2 = 3$ **(C)** $n_1 = 6,\ n_2 = 2$ **(D)** None of these

6. The frequency v of certain line of the Lyman series of the atomic spectrum of hydrogen satisfies the following conditions :

(i) It is the sum of the frequencies of another Lyman line and a Balmer line.

(ii) It is the sum of the frequencies of a certain line, a Balmer line and a Paschen line.

(iii) It is the sum of the frequencies of a Lyman and a Paschen line but no Brackett line.

To what transiton does v correspond?

(A) $n_2 = 3$ to $n_1 = 1$ **(B)** $n_2 = 3$ to $n_1 = 2$ **(C)** $n_2 = 2$ to $n_1 = 1$ **(D)** $n_2 = 4$ to $n_1 = 1$

7. Radiation corresponding to the transition n = 4 to n = 2 in hydrogen atoms falls on a certain alkali metal (work function = 2.0 eV). Calculate maximum kinetic energy (in eV) of the photoelectrons.

(A) 0.55 **(B)** 5.5 **(C)** 55 **(D)** None of these

8. Photochemical dissociation produces a normal oxygen atom and a oxygen atom 2.5 eV more energetic than normal one. Also the average bond energy of O_2 into normal oxygen is 498 kJ/mol. Determine the longest wavelength required for photochemical decomposition of O_2.

(A) 126 nm **(B)** 140 nm **(C)** 163 nm **(D)** 178 nm

Paragraph for Questions 9 - 12

Paragraph # 1 : One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the *n* = 1 orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state. If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value, in which case the atoms is in an excited with a higher energy.

The law of conservation of energy says that we cannot create or destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, then that same amount of energy will be liberated when the electron returns to its initial state.

Lyman series is formed when the electro returns to the lowest orbit while Balmer series is formed when the electron returns to second orbit. Similarly, Paschen, Brackett and Pfund series are formed when electrons returns to the third, fourth and fifth orbits from higher energy orbits respectively.

When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will equal to $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

If the electron comes back from energy level having energy E_1, then the difference may be expressed in terms of energy of photon as : $E_2 - E_1 = \Delta E,\ \Delta E \Rightarrow \frac{hc}{\lambda}$

Since, h and c are constants, ΔE corresponds to definite energy; thus, each transition from one energy level to another will produce a radiation of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Wave number of a spectral line is given by the formula $\overline{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ where R is a Rydberg's constant $\left(R = 1.1 \times 10^7\ m^{-1}\right)$.

Read the paragraph carefully and answer the following questions:

9. If the wavelength of series limit of Lyman series for He^+ ion is $x\ \mathring{A}$, then what will be the wavelength of series limit of Balmer series of Li^{2+} ion?

(A) $\frac{9x}{4}\mathring{A}$ **(B)** $\frac{16x}{9}\mathring{A}$ **(C)** $\frac{5x}{4}\mathring{A}$ **(D)** $\frac{4x}{7}\mathring{A}$

10. The emission spectra is observed by a consequence of transition of electron from higher energy state to ground state of He^+ ion. Six different photons are observed during the emission spectra, then what will be the minimum wavelength during the transition?

(A) $\frac{4}{27R_H}$ **(B)** $\frac{4}{15R_H}$ **(C)** $\frac{15}{16R_H}$ **(D)** $\frac{16}{15R_H}$

11. What transition in the hydrogen spectrum would have the same wavelength as Balmer transition, *n* = 4 to *n* = 2 in the He^+ spectrum?

(A) *n* = 3 to *n* = 1 **(B)** *n* = 3 to *n* = 2 **(C)** *n* = 4 to *n* = 1 **(D)** *n* = 2 to *n* = 1

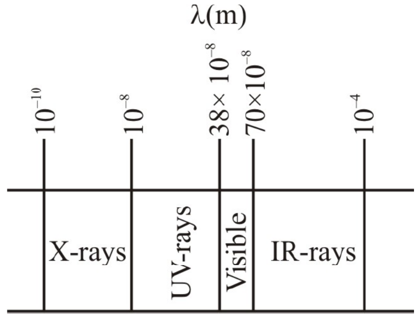
12. An electron in H-atom in M-shell on de-excitation to ground state gives …. spectrum lines.

(A) 10 **(B)** 6

(C) 3 **(D)** 1

Paragraph for Questions 13 - 16

Paragraph # 3 : The emission spectrum of H-atom and like species were studied by several scientists. All lines in UV region were studied by Lyman, all lines in visible region were studied by Balmer and the lines of longer wavelengths were studied by Paschen, Brackett and Pfund. The wavelength range of electromagnetic radiations are shown :



Read the paragraph carefully and answer the following questions :

13. For He^+, Lyman lines could be observed on spectrum when electron falls to :

(A) 1st Bohr orbit **(B)** 2nd Bohr orbit

(C) Either 1st or 2nd Bohr orbit **(D)** 1st, 2nd or 3rd Bohr orbit

14. For Li^{2+}, when an electron from a higher orbit falls to nth Bohr orbit. Visible lines would be observed. Here n is :

(A) 1 **(B)** 2

(C) 4 **(D)** 3

15. For He^+, when an electron falls from a higher orbit to nth orbit, all three types of lines i.e., UV, Visible and IR would be observed on the spectrum. Here, n could be :

(A) 1 **(B)** 2

(C) 3 **(D)** 4

16. Lines corresponding to which electronic transition in Li^{2+} ion would not be observed in the emission spectrum of H-atom?

(A) $6 \rightarrow 3$ **(B)** $8 \rightarrow 6$

(C) $9 \rightarrow 6$ **(D)** $12 \rightarrow 6$

Paragraph for Questions 17 - 19

Photon having wavelength 12.42 nm was allowed to strike a metal plate having work function 25 eV. Calculate the:

17. Maximum kinetic energy of photoelectrons emitted in eV.

(A) 76 Ev **(B)** 56 eV

(C) 7.6 eV **(D)** None of these

18. Wavelength of electron with maximum kinetic energy in Å.

(A) 14 Å **(B)** 1.4 Å

(C) 0.14 Å **(D)** None of these

19. Calculate the uncertainity in wavelength of emitted electron if the uncertainity in the momentum is 6.62×10^{-28} Kg m/sec. (h = 6.62×10^{-34} J- sec.) :

(A) 1.96×10^{-14} m **(B)** 0.96×10^{-14} m

(C) 19.6×10^{-14} m **(D)** None of these

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

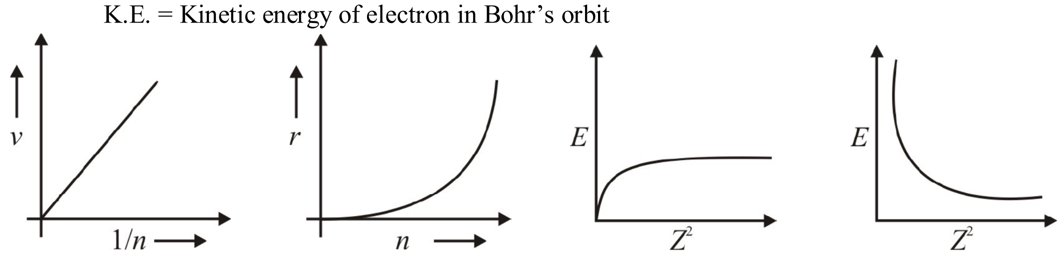
20. Select the correct curve (s) :

If v = Velocity of electron in Bohr's orbit [Assume n to be continuous value]

r = Radius of electron in Bohr's orbit

P.E. = Potential energy of electron in Bohr's orbit

K.E. = Kinetic energy of electron in Bohr's orbit



(A) **(B)** **(C)** **(D)**

21. A sample of hydrogen atoms absorbs radiation of wavelength λ_0 and consequently emits radiations of six different wavelengths of which three wavelengths are shorter than λ_0. Choose the correct alternatives.

(A) The highest orbit occupied by the electron is the fourth orbit.

(B) The initial orbit number of the electrons may be 2.

(C) The initial orbit number of the electrons may be 3.

(D) There are three transitions belonging to Lyman series

22. If the Binding energy of 2nd excited state of hypothetical H-like atom is $12\,eV$, then :

(A) Ist excitation potential $= 81\,V$

(B) II excitation energy $= 96\,eV$

(C) Ionisation potential $= 192\,V$

(D) Binding energy of 2nd state $= 27\,eV$

23. When photons of energy $4.25\,eV$ strike the surface of a metal A, the ejected photoelectrons have maximum kinetic energy $(K.E)_A$ and de-Broglie wavelength is λ_A. The maximum kinetic energy of photoelectrons liberated from another metal B by photons of energy $4.7\,eV$ is $(KE)_B$, where $(KE)_B = (KE)_A - 1.5\,eV$. If the de-Broglie wavelength of these photoelectrons is $\lambda_B (= 2\lambda_A)$, then :

(A) The work function of metal A is $2.25\,eV$

(B) The work function of metal B is $4.20\,eV$

(C) $(KE)_A = 2\,eV$

(D) $(KE)_B = 2.75\,eV$

24. Which of the following statements is/are INCORRECT:

(A) All spectral lines belonging to Balmer series in hydrogen spectrum lie in visible region

(B) If a light of frequency ν fall on a metal surface having work functional $h\nu$, photoelectric effect will take place only if $\nu \geq \nu_0$

(C) The number of photoelectrons ejected from a metal surface in photoelectric effect depends upon the intensity of intensity of incident radiations

(D) The series limit wavelength of Balmer series for H-atoms is $\frac{4}{R}$, where R is Rydber's constant

25. Which of the following statements are not correct about atomic orbital ?

(A) Size of the atomic orbital depends on the azimuthal quantum number

(B) Shape of the atomic orbital depends on both principal and azimuthal quantum number

(C) Orientation of an atomic orbital depends on the spin quantum number

(D) Rotation of an electron in an atomic orbital depends on Heisenberg uncertainty principle

26. Which of the following statement(s) is/are not a part of Bohr's model of hydrogen atom ?

(A) Splitting of spectral lines takes place in electric and magnetic field

(B) Energy of the electron in the orbit is not quantized

(C) Angular momentum of the electron in the orbit is quantized

(D) The radius and velocity of the electron in the orbit can be determined simultaneously

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

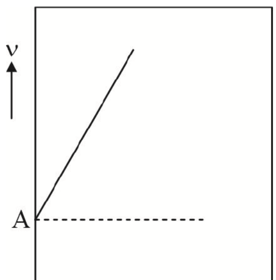
27. Calculate the number of waves made by a Bohr electron in one complete revolution in n^{th} orbit of H-atom, if ratio of de-Broglie wavelength associated with electron moving in nth orbit and 2^{nd} orbit is 3 : 1.

28. What is the total number of radial and angular nodes present in 5f orbital?

29. Given that, $r_{(n+1)} - r_n = r_{(n-1)}$, where r_n, r_{n-1} and r_{n+1} are Bohr's radius for H-atom in n^{th}, $(n-1)^{th}$ and $(n+1)^{th}$ shell respectively, then find the value of n.

30. The electron in the first excited state ($n_1 = 2$) of H-atom absorbs a photon and is further excited (n_2).The De-Broglie wavelength of the electron in this excited state is 1340 pm. Find the value of n_2.

31. Photoelectric effect can be expressed in terms of the following graph : [Given $h = 6.62 \times 10^{-34}$ Js]



Value of intercept $= 5 \times 10^{14} s^{-1}$

What is work function in kJ / mole for this photoelectric emission of electrons ?

32. If the photon of wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of $1.5 \times 10^7 ms^{-1}$, then binding energy by which electron is bound to nucleus is $x \times 10^{-15}$ J. The numerical value of x is________. Plank's constant $= 6.62 \times 10^{-34}$ Js, $C = 3 \times 10^8 ms^{-1}$, $m_e = 9.11 \times 10^{-31}$ kg)

33. The position of both, an electron and a helium atom is known within 1.0 mm.

Further more the momentum of the electron is known with $5.0 \times 10^{-26} \, kg \, ms^{-1}$.

The minimum uncertainly in the measurement of the momentum of the helium atom is $x \times 10^{-26} \, kg \, ms^{-1}$. The numerical value of x is________.

34. An electron in H-atom in its ground state absorbs 1.5 times as much as energy as the minimum required for its escape from the atom.

$$H(g) \longrightarrow H^{+}(g) + e^{-}; \quad \Delta H = 13.6 \, eV \, atom^{-1}$$

Thus, kinetic energy in eV of the emitted electron is________.

35. Consider the following dissociation of O_2 (dissociation energy $498 \, kJ \, mol^{-1}$)

$$O_2 \xrightarrow{hv} O + O^*$$

O* is more energetic than normal oxygen atom (O) by $1.967 \, eV$. The maximum wavelength in nm for photochemical dissociation is ________. (Given : $N_A = 6.02 \times 10^{23} \, J \, mol^{-1}$, $h = 6.62 \times 10^{-34}$ Js, $C = 3 \times 10^{8} \, ms^{-1}$)

Advanced Problem Package	Gaseous State

SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. In the reaction : $CO + \frac{1}{2}O_2 \rightarrow CO_2;\ N_2 + O_2 \rightarrow 2NO$

10 mL of mixture containing carbon monoxide and nitrogen required 7 mL of oxygen to form CO_2 and NO on combustion. The volume of N_2 in the mixture will be :

(A) 7/2 mL **(B)** 17/2 mL **(C)** 4 mL **(D)** 7 mL

2. Pay load is defined as, the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and R = 0.083 bar dm^3K^{-1} mol^{-1}).

(A) 3602.35 kg **(B)** 3811.1 kg **(C)** 3204.89 kg **(D)** 3807.54 kg

Paragraph for Questions 3 - 4

Kinetic theory of gases is a generalization offered by Maxwell, Boltzman, Clausius, etc., to explain the behavior of ideal gases. This theory assumes that ideal gas molecules neither attract nor repel each other. Average kinetic energy of a gas molecules is directly proportional to the absolute temperature. A gas equation called kinetic gas equation was derived on the basis of kinetic theory.

$$PV = \frac{1}{3}mnv^2$$

3. The average kinetic energy per molecule of an ideal gas is equal to :

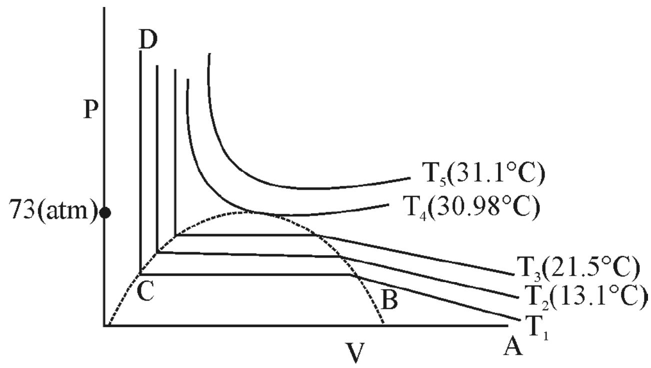
(A) 0.5 kJ **(B)** 0.5 RT **(C)** 1.5 KT **(D)** 1.5 RT^2

4. Which of the following do not pertain to the postulates of kinetic theory of gases?

(A) No loss in kinetic energy during collision.
(B) Speed of gas molecules are ever changing.
(C) Pressure exerted by the gas is due to the collision of molecules with the walls of the container.
(D) Kinetic energy of a gas is given by the sum of 273 and temperature in Celsius scale.

Paragraph for Questions 5 - 7

For an ideal gas P, V curve is hyperbola but for any real gas the curves show variation. Andrew has observed the curve for CO_2 and concluded that other real gases also show similar curve. At high temperature real gas behaves similar to an ideal gas. Answer following questions on the given information.



5. The gas can't be liquefied when :

I. Pressure is greater than 73 at 30.98°C
II. Pressure is smaller than 73 at 30.98°C
III. Both P and T are greater than 73 and 30.98 respectively.
IV. At T_2 temperature pressure applied is 73

(A) TTTT **(B)** FTTF **(C)** TFTF **(D)** FFTT

6. For the curve ABCD. The vapour pressure is given by :

(A) Pressure corresponding to any point for AB **(B)** Pressure corresponding to any point for CD

(C) Pressure corresponding to any point for BC **(D)** Pressure corresponding to any point from A to D

7. The highest temperature at which the gas can be obtained in liquid state is :

(A) 31.1 **(B)** 30.98

(C) 13.1 **(D)** 21.5

8. 'a' and 'b' are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because

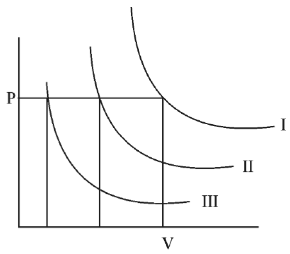
(A) a and b for Cl_2 > a and b for C_2H_6

(B) a and b for Cl_2 < a and b for C_2H_6

(C) a for Cl_2 < a for C_2H_6 but b for Cl_2 > b for C_2H_6

(D) a for Cl_2 > a for C_2H_6 but b for Cl_2 < b for C_2H_6

9. I, II, III are three isotherms respectively at T_1, T_2 and T_3. Temperature will be in order :



(A) $T_1 = T_2 = T_3$

(B) $T_1 < T_2 < T_3$

(C) $T_1 > T_2 > T_3$

(D) $T_1 > T_2 = T_3$

10. A 0.5 dm^3 flask contains gas A and 1 dm^3 flask contains gas B at the same temperature. If density of A = 3.0 g dm^{-3} and that of B = 1.5 g dm^{-3} and the molar mass of A $= \frac{1}{2}$ of molar mass of B, then the ratio of pressure exerted by gases is :

(A) $\frac{P_A}{P_B} = 2$ **(B)** $\frac{P_A}{P_B} = 1$

(C) $\frac{P_A}{P_B} = 4$ **(D)** $\frac{P_A}{P_B} = 3$

11. The total kinetic energy of a sample of gas which contains N molecules at –123°C is E_K Joules. Another sample of gas at 27°C has total kinetic energy $2E_k$ Joules. The number of molecules in the second sample of gas is :

(A) N/2 **(B)** 2N **(C)** N **(D)** N^2

12. A solid P is kept in a sealed vessel containing He gas at 1 atm. at 27°C. The vessel is heated to 127°C such that all the solid P sublimes and the total pressure increases to 2atm. On further heating to 327°C, gaseous P further dissociates as per the reaction: $P(g) \longrightarrow Q(g) + R(g)$

Final pressure in the vessel will be :

(A) 2 atm **(B)** 3 atm **(C)** 3.33 atm **(D)** 4 atm

13. The compressibility factor of N_2 at 330K and 800 atm is 1.90 and at 570K and 200 atm is 1.10. A certain mass of N_2 occupies a volume of 1dm^3 at 330K and 800 atm. Calculate the volume of N_2 gas at 570K and 200 atm.

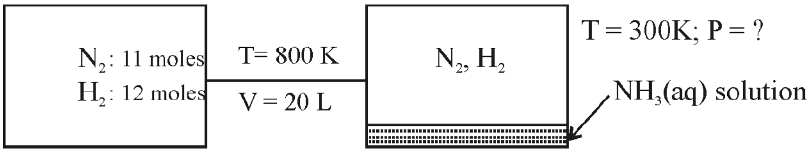
(A) 1 L **(B)** 2 L **(C)** 3 L **(D)** 4 L

14. The density of O_2 is maximum at :

(A) STP **(B)** 273 K and 2 atm

(C) 546K and 1 atm **(D)** 546 K and 2 atm

15. 11 moles N_2 and 12 moles of H_2 mixture reacted in 20 litre vessel at 800 K. After equilibrium was reached, 6 mole of H_2 was present. 3.58 litre of liquid water is injected in equilibrium mixture and resultant gaseous mixture suddenly cooled to 300 K. What is the final pressure of gaseous mixture? Neglect vapour pressure of liquid solution. Assume (i) all NH_3 dissolved in water (ii) no change in volume of liquid (iii) no reaction of N_2 and H_2 at 300 K.



Initial condition :

(A) 18.47 atm **(B)** 60 atm **(C)** 22.5 atm **(D)** 45 atm

16. Two closed vessel A and B of equal volume containing air at pressure P_1 and temperature T_1 are connected to each other through a narrow open tube. If the temperature of one is now maintained at T_1 and other at T_2 (where $T_1 > T_2$) then what will be the final pressure :

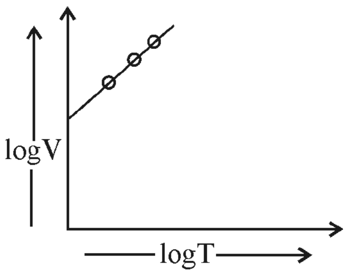
(A) $\frac{T_1}{2P_1T_2}$ **(B)** $\frac{2P_1T_2}{T_1+T_2}$ **(C)** $\frac{2P_1T_2}{T_1-T_2}$ **(D)** $\frac{2P_1}{T_1+T_2}$

MULTIPLE CORRECT ANSWERS TYPE

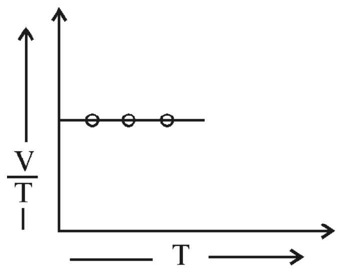
Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

17. Which of the following plots represents Charles' law ?

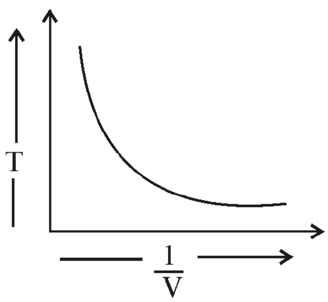
(A)



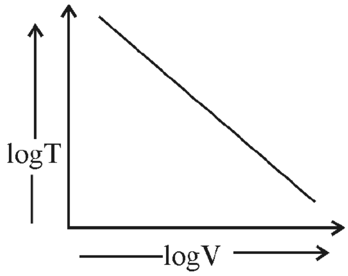
(B)



(C)



(D)



18. In a closed flask of 5L, 1.0 g of H_2 is heated from 300 K to 600 K. Which statements are correct :

(A) The rate of collision increases

(B) The energy of gaseous molecules increases

(C) The number of moles of the gas increases

(D) Pressure of the gas increases

19. The root mean square velocity of an ideal gas in a closed container of fixed volume is increased from 5×10^4 cm s^{-1} to 10×10^4 cm s^{-1}. Which of the following statements correctly explains how the change is accomplished?

(A) by heating the gas, the temperature is doubled
(B) by heating the gas, the pressure is quadrupled
(C) by heating the gas, the pressure is doubled
(D) by heating the gas, the temperature is quadrupled

20. Select the correct statement(s):

(A) At the limit of vanishing pressure, where all gases behave ideally, the volume tends to infinity and intermolecular distances becomes enormously large
(B) Gases with weak intermolecular forces obey the ideal gas law at relatively high pressures
(C) Gases with strong intermolecular forces obey the ideal gas law at relatively low pressures
(D) All the statements are incorrect

21. If temperature of a gas is raised, which of the following would be true?

(A) Fraction of the molecules possessing most probable velocity will increase
(B) Fraction of the molecules possessing most probable velocity will decrease
(C) Fraction possessing very low velocity will decrease
(D) Fraction possessing very high velocity will increase

22. Select the correct statement regarding the vander waal real gas :

(A) At low pressure $z = 1 + \frac{Pb}{RT}$
(B) More is the value of vander waal's constant 'a' easier will be the liquification of gas
(C) Boyle temperature is more than critical temperature
(D) $P_C = \frac{8a}{27Rb}$

23. Which of the following is(are) correct for a gas obeying vander waal's equation?

(A) A gas having negligible size and reasonable intermolecular force follow $\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$
(B) A gas having negligible intermolecular force and reasonable size follow: $Z = 1 - \frac{Pb}{RT}$
(C) A gas having negligible size and negligible intermolecular force follow $PV_m = RT$
(D) At Boyle's temperature, gas follow $PV_m = RT$ at all pressure

24. Which of the following statement is correct about mean free path:

(A) λ remains unchanged on heating the gas in a closed container
(B) λ remains constant on heating the gas in a closed rigid container
(C) On increasing the T, λ increases (P and n constant)
(D) λ is inversely proportional to T

25. An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that 2/3 rd of air measure at final temperature escapes out.

(A) 400 K **(B)** 450 K
(C) 500 K **(D)** 227°C

26. Which of the following equation can't be obtained from Vander waal's equation for Z at proper conditions :

(A) $1+\frac{a}{RTV_m}$ **(B)** $1+\frac{Pb}{RT}$ **(C)** $1-\frac{a}{RTV_m}$ **(D)** $1-\frac{Pb}{RT}$

27. A gas at 250 K and 15 atm has a molar volume 12% smaller than that calculated from ideal gas low, find the correct option for the above condition :

(A) Z = 0.90 **(B)** V_m = 1.2 L

(C) 'b' is dominating **(D)** 'a' is dominating

28. Select the correct statement about Vander Waal's constant 'b':

I. It is excluded volume **II.** Its unit is L/mol

III. It depends on intermolecular force **IV.** Its value depends on molecular size

(A) II, III **(B)** I, II, IV

(C) II, III, IV **(D)** III, IV

29. Precisely 1 mole of Helium and 1 mole of Neon are placed in a container at same temperature. Indicate the correct statements about the system:

(A) Molecules of the two gases strike the wall of the container with same pressure

(B) Molecules of Helium & Neon have same average molecular speed

(C) Molecules of Helium has greater average molecular speed

(D) Helium exerts larger pressure as compared to Neon

30. If 10 gm of a gas at atmospheric pressure is cooled from 273°C to 0°C, keeping the volume constant, its pressure would become :

(A) $\frac{1}{273}$ atm **(B)** 2 atm

(C) $\frac{1}{2}$ atm **(D)** $5.05\times10^4\ N/m^2$

31. The compressibility of a gas is greater than unity at S.T.P. Therefore,

(A) $V_m > 22.4$ litres **(B)** $V_m < 22.4$ litres

(B) $V_m = 22.4$ litres **(D)** the gas will become less liquefiable

32. Select correct statements :

(A) Vapour may be condensed to liquid by the application of pressure

(B) To liquefy a gas one must lower the temperature below T_c and apply pressure

(C) At T_c there is no distinction between liquid and vapour state

(D) At T_c density of liquid is very high as compared to its gaseous state

33. Which of the following statement is/are correct ?

(A) All real gases are less compressible than ideal gas at high pressure

(B) Hydrogen and Helium are more compressible than ideal gas for all values of pressure

(C) Except H_2 and He, the compressibility factor $Z=\left(\frac{PV}{nRT}\right)<1$ for all gases at low pressure

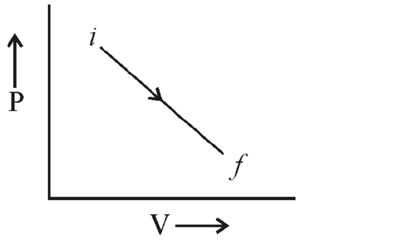
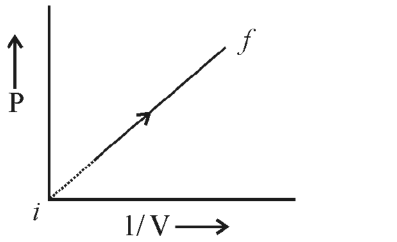
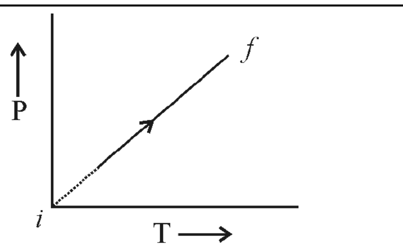
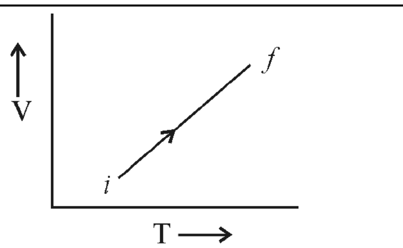
(D) The compressibility factor of real gases is independent of temperature

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labeled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

34. MATCH THE FOLLOWING:

A system is proceeding from initial state to final state by different ways column I shows diagrams for processes match it with column II (i.e. initial state, *f* = final state)

Column 1		Column 2	
(A)		**(p)**	Temperature will remain constant
(B)		**(q)**	Pressure will remain constant
(C)		**(r)**	Volume will be constant
(D)		**(s)**	Temperature may increase or decrease or may first increased and then decrease.

35. MATCH THE FOLLOWING: (For an ideal gas)

Column 1		Column 2	
(A)	If temperature of given gas is increased	**(p)**	Average speed of gas will increase
(B)	If pressure of a given gas is increased at constant temperature	**(q)**	Root mean square speed of gas molecules will increase
(C)	If the density of a given gas is lowered at constant temperature	**(r)**	Must probable speed of gas molecules will increase
(D)	If the volume of a given gas is increased at constant temperature	**(s)**	Speed of gas molecules will not change.

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

36. Consider 40 mL of a gaseous mixture of CO, CH_4 and Ne that was exploded with 10 mL O_2. On cooling, the gases occupied 36.5 mL. After treatment with KOH, the volume reduced by 9 mL and again on treatment with alkaline pyrogallol, the volume further reduced. Find the volume (in mL) of CH_4.

37. 16 mL of gaseous hydrocarbon when exploded with excess oxygen and then cooled, there was a contraction of 48 mL. On passing through KOH solution, there was a further contraction of 48 mL. Find the number of Carbon atoms in hydrocarbon.

38. Two vessels of volumes 16.4 L and 5 L contain two ideal gases of molecular existence at the respective temperature of 27°C and 227°C and exert 1.5 and 4.1 atmospheres respectively. The ratio of the number of molecules of the former to that of the later is __________.

39. The excluded volume of a molecule in motion is x times the actual volume of a molecule in rest. The value of x is __________.

40. If the ratio of masses of SO_3 and O_2 gases confined in a vessel is 1:1, then the sum of the ratio of their partial pressure would be ______.

41. Under identical condition of temperature and pressure, one litre of CH_4 weighed 1.2 g while 2 litre of another gaseous hydrocarbon C_nH_{2n-2} weighed 8.1 g. The value of n is _________.

42. The stopcock, connecting the two bulbs of volumes 5 litres and 10 litres containing an ideal gas at 9 atm and 6 atm respectively, is opened. The final pressure in the two bulbs if the temperature remained the same is __________.

43. At 400 K the root mean square (rms) speed of a gas x. (mol. wt. 40) is equal to the most probable speed of gas y at 60 K. The mol. wt. of the gas y is __________.

44 A sample of water gas has a composition by volume of 50% H_2, 45% CO and 5% CO_2. Calculate the volume in litre at S.T.P. of water gas which on treatment with excess of steam will produce 5 litre H_2. The equation for the reaction is :

$$CO + H_2O \longrightarrow CO_2 + H_2$$

45 The rate of diffusion of a sample of ozonised oxygen is 0.98 times than that of oxygen. Find the percentage (by volume) of ozone in the ozonised sample.

46 Consider the reaction

$$2X(g) + 3Y(g) \longrightarrow Z(g)$$

Where gases X and Y are insoluble and inert to water and Z form a basic solution. In an experiment 3 mole each of X and Y are allowed to react in 15 lit flask at 500 K. When the reaction is complete, 5L of water is added to the flask and temperature is reduced to 300 K. The pressure in the flask is (neglect aqueous tension)________atm. [Given : $R = 0.0821\,L\,atm^{-1}\,mol^{-1}\,K^{-1}$]

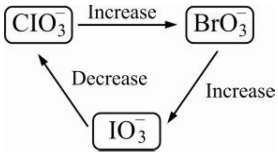
47 A mixture of carbon monoxide and carbon dioxide is found to have a density of 1.7 g/lit at S.T.P. The mole fraction of carbon monoxide is________. [Given : $R = 0.0821\,L\,atm\,mol^{-1}\,K^{-1}$]

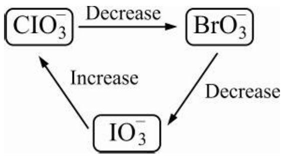
Advanced Problem Package	Chemical Bonding

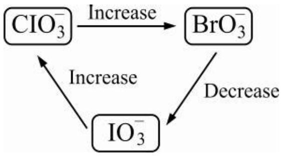
SINGLE CORRECT ANSWER TYPE

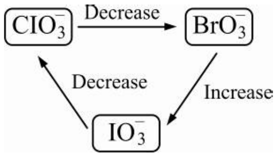
Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. Select diagram which represent the correct change in the bond angle of given ions.

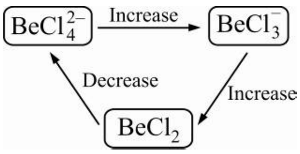
(A) 

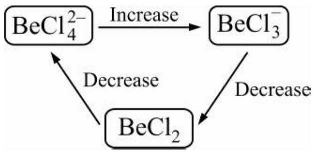
(B) 

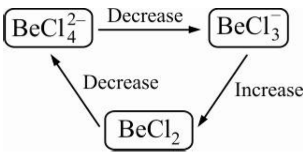
(C) 

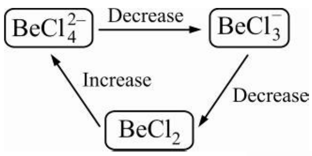
(D) 

2. Select systematic diagram which represent the correct change in the % s-character in the hybrid orbital of beryllium.

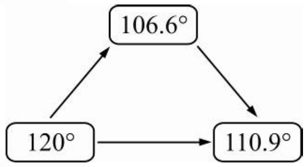
(A) 

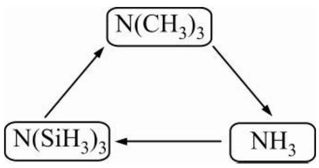
(B) 

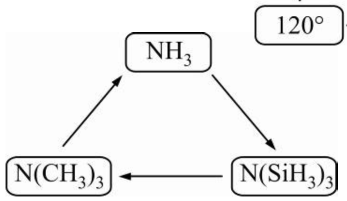
(C) 

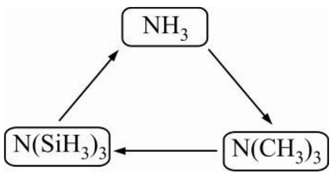
(D) 

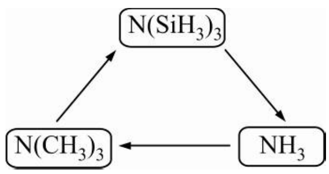
3. In which of the following diagram the change in the bond angle at nitrogen is observed as



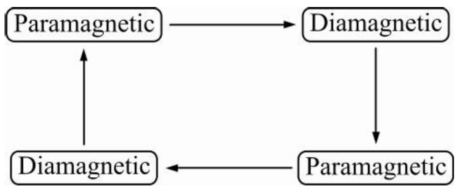
(A) 

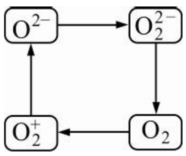
(B) 

(C) 

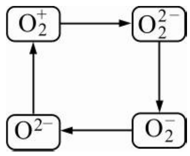
(D) 

4. In which of the following diagram magnetic nature of species is changed as :

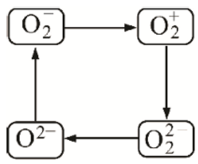




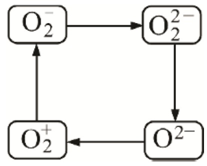
(A)



(B)



(C)



(D)

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

5. In which pair first compound has more dipole moment than second compound?

(A) $P(CH_3)_2(CF_3)_3$, $P(CH_3)_3(CF_3)_2$ **(B)** CH_3Cl, CH_3F

(C) NH_3, NF_3 **(D)** Benzene, Borazine

6. In which of the following hybridisation lone pairs are not observed on opposite position?

(A) sp^3 **(B)** sp^3d **(C)** sp^3d^2 **(D)** sp^3d^3

7. Which of the following will result in zero overlap if molecular axis is x-axis?

(A) $1s-2p_x$ **(B)** $2s-2p_z$ **(C)** $2p_x-2p_x$ **(D)** $1s-2p_y$

8. If the molecular axis is z-axis, then which of the following sets of orbitals are not affected by s – p mixing for N_2 molecule?

(A) $\sigma 2s, \sigma 2p_z$ **(B)** $\pi 2p_x, \pi 2p_y$

(C) $\sigma 2s, \sigma^* 2s$ **(D)** $\pi^* 2p_x, \pi^* 2p_y$

9. Select correct statement for AB_nL_2 :

[A = central atom; L = lone pair of electron on A; n = number of monovalent atom B]

(A) Molecule will be planar and non polar when n = 4

(B) Molecule will be non planar and polar when n = 3

(C) Molecule will be planar and polar when n = 2

(D) Bond polarity is equal to molecular polarity when n =2

10. Which of the following has planar geometry in both monomeric and dimeric forms?

(A) ICl_3 **(B)** $AlCl_3$ **(C)** NO_2 **(D)** BH_3

11. In which case bond energy decreases from left to right?

(A) N_2, P_2, As_2, Sb_2 **(B)** F_2, Cl_2, Br_2, I_2

(C) O_2, S_2, Se_2, Te_2 **(D)** C_2, N_2, O_2, F_2

12. Select correctly matched.

(A) $Cr_2O_7^{2-} \Rightarrow$ two tetrahedral units are joined by their common corner

(B) $S_2O_6^{2-} \Rightarrow$ centre of one tetrahedral is the corner of other tetrahedral

(C) $S_2F_{10} \Rightarrow$ two octahedral joined together

(D) $S_2O_8^{2-} \Rightarrow$ two tetrahedral unit joined by their corners

13. In which of the following geometry of underlined atom is not changed on replacing all $-CH_3$ groups by $-SiH_3$?

(A) $(CH_3)_3\underline{N}$ **(B)** $H_3C\underline{N}CO$

(C) $H_3C\underline{O}CH_3$ **(D)** $(CH_3)_3\underline{P}$

14. $H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$ (urea), $HO-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ (carbonic acid), $F-\overset{\overset{\displaystyle O}{\|}}{C}-F$ (carbonyl fluoride) have :

(A) different number of total lone pair **(B)** different number of total bond pairs

(C) same number of electrons **(D)** same number of σ - bond pairs

15. Which of the following is(are) iso-structural pairs?

(A) B_2H_6, C_2H_6 **(B)** Al_2Cl_6, C_2Cl_6

(C) B_2H_6, Al_2Cl_6 **(D)** C_2H_6, C_2Cl_6

16. Which is(are) not exist?

(A) B_2 **(B)** C_2 **(C)** Be_2 **(D)** Li_2

17. The bond order in O_2^+ is the same as in:

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

18. The diamagnetic molecules are :

(A) B_2, C_2, N_2 **(B)** O_2, N_2, F_2 **(C)** C_2, N_2, F_2 **(D)** B_2, O_2^{2-}, N_2

19. The species having diamagnetic nature and bond order 1.0 is(are) :

(A) O_2^{2-} **(B)** O_2^+ **(C)** O_2^{2+} **(D)** O_2

20. The species which does not show paramagnetism is(are):

(A) O_2 **(B)** O_2^+ **(C)** O_2^{2-} **(D)** H_2^+

21. Which of the following molecule has/have only σ type covalent bond between two non metallic atoms?

(A) CaC_2 **(B)** CsO_2 **(C)** Na_2O_2 **(D)** F_2

22. When N_2 is ionised to N_2^+, bond length ……. and if O_2 is ionised to O_2^+, bond length…… (Select correct option to fill the blank space respectively):

(A) Increases and decreases **(B)** Decreases and increases

(C) Increases and increases **(D)** Decreases and decreases

23. In which species the hybrid state of central atom is(are) sp^3d ?

(A) I_3^+ **(B)** SF_4 **(C)** PF_5 **(D)** IF_5

24. A molecule XY_2 contains two σ, two π-bonds and one lone pair of electron in the valence shell of X. The arrangement of lone pair and bond pairs is:

(A) Square pyramidal **(B)** Linear
(C) Trigonal planar **(D)** Unpredictable

25. Which of the following pairs of species have identical shapes?

(A) NO_2^+ and NO_2^- **(B)** PCl_5 and BrF_5 **(C)** XeF_4 and ICl_4^- **(D)** $TeCl_4$ and XeO_4

26. Indicate the wrong statement(s) :

(A) A sigma bond has no free rotation along its axis
(B) p-orbitals always have only sidewise overlapping
(C) s-orbitals never form π-bonds
(D) There can be more than one sigma bond between two atoms

27. Which of the following molecules or ions is(are) linear?

(A) $BeCl_2$ **(B)** ICl_2^- **(C)** CS_2 **(D)** ICl_2^+

28. Assume that BrF_3 in liquid phase intermolecularly exchanges one F^- ion to give an ion pair, then which of the following statement(s) is(are) correct?

(A) Cation is sp^3 hybrid and anion is sp^3d^2 hybrid **(B)** Cation and anion both are planar
(C) Cation is non-planar and anion is planar **(D)** Cation is planar and anion is non-planar

29. Select correct statement(s).

(A) All $N-N$ bond length are same in N_3^- (Azide) ion
(B) All $N-N$ bond length are not identical in HN_3 (Hydrazoic acid)
(C) In HN_3 terminal $N-N$ bond length is shorter that the central $N-N$ bond length
(D) Azide ion and hydrazoic acid have same number of electron

Paragraph for Questions 30 - 32

Bond formation between two atoms is then envisaged as the progressive overlapping of an atomic orbital from each of the participating atoms, the greater the overlap achieved (the overlap integral), the stronger the bond so formed.

30. For σ bond formation the relative overlapping power of:

(A) s-orbital is greater than p-orbital because s-orbital are closer to nucleus
(B) p-orbitals is greater than s-orbital because p-orbitals are far away from nucleus
(C) s-orbital is greater than p-orbital because of spherical shape of s-orbital
(D) p-orbital is greater than s-orbital because electrons of p-orbitals are oriented on internuclear axis

31. In which of the following pair both have similarity in bond angle(s) between adjacent chlorine?

(A) $PCl_3, PCl_4^{\oplus}$ **(B)** $PCl_4^{\oplus}, PCl_5$ **(C)** $PCl_5, PCl_6^{\ominus}$ **(D)** $PCl_4^{\oplus}, PCl_6^{\ominus}$

32. In inorganic benzene ($B_3N_3H_6$) :

(A) Only six $(sp^2-sp^2)\sigma$ bonds and three $p\pi-p\pi$ coordinate bond
(B) Twelve $(sp^2-sp^2)\sigma$ bonds and three $p\pi-p\pi$ coordinate bond
(C) Six $(sp^2-sp^2)\sigma$ bonds, six $(sp^2-s)\sigma$ bonds and three $p\pi-p\pi$ coordinate bond
(D) Six $(sp^2-sp^2)\sigma$ bonds, six (sp^2-sp^2) coordinate π-bond

Paragraph for Questions 33 - 34

The shape of a molecule is determined by the number of groups of electrons around the central atom. The 'groups' might be a non-bonding single electron, a non-bonding or bonding pair of electrons, a double pair of bonding electrons or triple pair of bonding electrons etc. The electron 'groupings' minimise the repulsion to decrease potential energy of the system i.e., to make the Q – X – Q angle as wide as possible. (X = central atom, Q = surrounding atom).

According to VSEPR theory repulsive interaction are summarized as lone pair – lone pair > lone pair – bond pair > bond pair – bond pair. So that as the lone pair – 'other pair repulsion increases, the angle between these pairs increases, so the Q – X – Q angle will be slightly reduced compared to what might be expected from the simple geometry or shape.

33. In which of the following pair both species have same Cl – X – Cl bond angle?

I. CCl_4, $SiCl_4$ **II.** $POCl_3$, SO_2Cl_2 **III.** BCl_3, $AlCl_3$ **IV.** $SOCl_2$, $COCl_2$

(A) I, II **(B)** III, II, I **(C)** I, III **(D)** II, IV

34. In which of the following species presence of L.P does not affect idealized bond angle?

I. PF_3 **II.** BrF_3 **III.** IF_5 **IV.** ICl_4^- **V.** XeF_2

(A) I, II, III **(B)** IV, V **(C)** II, V **(D)** None of these

Paragraph for Questions 35 - 37

The mixing or redistribution of energy among the atomic orbitals is known as hybridisation. In hybridisation each electron can be described by its wave function ψ.

35. Which of the following set of species has same electronic geometry?

(A) PCl_3, NH_3, SO_3 **(B)** CH_4, NH_3, H_2O **(C)** ClF_3, BF_3, NF_3 **(D)** CO_2, SiO_2, SO_2

36. In which of the following species lone pair-bond pair repulsion is maximum?

(A) NH_3 **(B)** NF_3 **(C)** SF_4 **(D)** NO_2^-

37. BF_3 form adduct with NH_3 as Lewis acid-base reaction, in which atom hybridisation will change?

(A) Both N and B **(B)** Only B not N **(C)** Only N not B **(D)** None of these

Paragraph for Questions 38 - 40

Xe reacts with F_2 at different ratio to give different types of xenon fluorides.

$$\underset{(2\ :\ 1)}{Xe + F_2} \longrightarrow XeF_2 \quad ; \quad \underset{(1\ :\ 5)}{Xe + F_2} \longrightarrow XeF_4 \quad ; \quad \underset{(1\ :\ 20)}{Xe + F_2} \longrightarrow XeF_6$$

38. Which of the following option is correct regarding XeF_2?

(A) Two fluorine occupy equatorial position

(B) There are total two bond pair and two lone pair present in XeF_2

(C) Its structure is linear and it is isostructural with I_3^-

(D) Hybridisation of XeF_2 is sp^3

39. The shape and hybridisation of XeF_4 is :

(A) tetrahedral and sp^3 **(B)** square pyramidal and sp^2d

(C) square planar and sp^3d **(D)** square planar and sp^3d^2

40. In XeF_6 the number of lone pair and bond pair is respectively and its hybridisation is :

(A) 0, 6 ; sp^3d^2 **(B)** 1, 6; sp^3d^3 **(C)** 0, 5; sp^3d **(D)** 1,5;sp^3d^2

Paragraph for Questions 41 - 43

Bond Length : Internuclear distance between two adjacent atoms in a species is known as bond length. Bond length depends on:

(i) Size of the atom involved in the bond formation

(ii) Size of the orbitals involved in the bond formation

(iii) Lone pair-lone pair repulsion **(iv)** Resonance **(v)** s-character of combining orbital

With the increasing size of the atoms and atomic orbitals bond length increase. Lone pair repulsion increases bond length (if atoms are small sized) whereas resonance can increase some bond lengths and decrease some other bond length. With increasing s-character bond length decreases, whereas with increasing multiplicity of bonds, bond length decreases. However, in some cases, bond lengths are also affected by relative position of bonds (between two similar atoms). Usually but not always with increasing bond length, bond strength (and hence bond dissociation energy) decreases.

41. The correct order B – F bond length follows the sequence :

(A) $BF_3 < BF_2OH < BF_2NH_2 < BF_4^-$ **(B)** $BF_2NH_2 < BF_2OH < BF_3 < BF_4^-$

(C) $BF_3 < BF_4^- < BF_2OH < BF_2NH_2$ **(D)** $BF_3 < BF_2NH_2 < BF_2OH < BF_4^-$

42. Consider the following statements :

I. Percentage of σ - bonding in $C-O$ bond follows the sequence $CO < CO_2 < CO_3^{2-}$

II. Relative strength of π – bonding in BX_3 $(X - F, Cl, Br, I)$ follows the sequence $BF_3 = BCl_3 > BBr_3 > BI_3$

III. The correct order of bond length $(S-O)$ follows the sequence $SO_3 < SO_4^{2-}$

IV. π - bond order follows the sequence $ClO_2^- > ClO_3^- > ClO_4^-$

Using 'T' for 'True' and 'F' for 'False' statement in the given sequence, pick the correct set of codes.

(A) TFTT **(B)** TFTF **(C)** TTFT **(D)** FTTF

43. In which of the following all bonds are not equivalent?

(A) N_2O **(B)** CN_2^{2-} **(C)** N_3^- **(D)** NO_2^-

Paragraph for Questions 44 - 46

There are some cases in which the number of available valency electrons is not sufficient to displays the normal electron pair bonds (i.e., 2 centre-2 electron, $2c-2e^-$) among all the constituent atoms. This type of compounds is generally referred to as electron deficient compounds. Here it is worth nothing that in a particular compound, all the bonds are not to be necessarily electron deficient. The occurrence of electron deficient covalent bonds is a common feature in some classes of compounds of group IIIA elements. For example, boron contains only three valence electron and it stands as a typical example of electron deficient atoms.

Retaining the valence bond concept of relationship between bond distance and bond order we encounter a problem on examining the known structure of some electron deficient compound like diborane. Satisfactory theories of bonding in electron deficient compounds introduce the concept of $3c-2$ electron bond. A simple extension to include $3c-2e$ bond explain many electron deficient compound.

44. Select correct statement about B_2H_6 (diborane) and C_2H_6 (ethane).

(A) B_2H_6 has total 12 valence electrons but C_2H_6 has total 18 valence electrons

(B) Each compound contains four identical $M-H$ bonds (M = B or C)

(C) Every sp^3 orbital of central atom in B_2H_6 is associated with H but not so in C_2H_6

(D) Free rotation around central atoms is possible in both

45. Molecule in which three centred two electron bond present is :

I. Si_2H_6 **II.** C_2H_4 **III.** P_2H_4 **IV.** Be_2H_4

(A) III and IV **(B)** I, II and III **(C)** Only IV **(D)** I and IV

46. Select correct statement about solid BeH_2 and solid $BeCl_2$.

(A) Both have similar structure but different bonding

(B) Both have similar bonding but different structure

(C) Both have similar bonding and structure

(D) Both have different bonding and structure

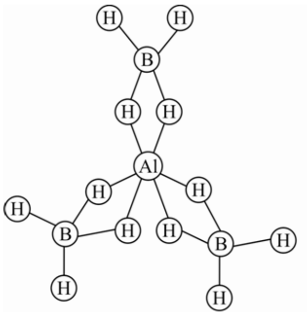
Paragraph for Questions 47 - 49

47. Select incorrect statement about $Li[AlH_4]$.

(A) Hybridistation of Al is same as B in $Na[BH_4]$ **(B)** Geometry around Al is same as $AlCl_4^-$

(C) $AlH_4^-, BH_4^-, AlCl_4^-$ are iso-structural **(D)** $AlH_4^-, AlCl_4^-, BH_4^-$ are iso-electric

48. Select correct about $Al(BH_4)_3$:



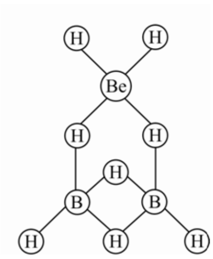
(A) Each tetrahydride borate form two hydrogen bridges

(B) Two BH_4 form 2 hydrogen bridges and one BH_4^- form one hydrogen bridge

(C) One BH_4^- form 2 hydrogen bridge and two BH_4^- form one hydrogen bridge

(D) B form only $2c-2e$ bond

49. Total $2c-2e$ and $3c-2e$ bonds in $Be(BH_4)_2$ are respectively :



(A) 6, 4

(B) 4, 6

(C) 4, 4

(D) 4, 8

50. Which of the following is not correct?

(A) During N_2^+ formation, one electron is removed from the bonding molecular orbitals

(B) During O_2^+ formation, one electron is removed from the antibonding molecular orbital

(C) During O_2^- formation one electron is added to the bonding molecular orbital

(D) During CN^- formation one electron is added to the bonding molecular orbital

51. Which of the following pairs have identical bond order?

(A) N_2^+ and O_2^+ **(B)** F_2 and Ne_2 **(C)** O_2 and N_2 **(D)** C_2 and N_2

52. Among the following the incorrect statement:

(A) NO has one unpaired electron in the antibonding molecular orbital

(B) Bond length of $NO > NO^+$

(C) Magnetic moment of N_2^+ is $\sqrt{3}$ B. M.

(D) Magnetic moment of O_2 is zero

Paragraph for Questions 53 - 55

Hydrogen bonding is said to be formed, when slightly acidic hydrogen atom attached to a strongly, electronegative fluorine, oxygen or nitrogen atom, is held with weak electrostatic forces by the non-bonded pair of electrons of another atom. The co-ordination number of hydrogen in such cases is two. It acts as a bridge between two atoms, to one of which it is covalently bonded and to other attached through electrostatic forces, also called Hydrogen bond.

Though the hydrogen atoms in a methyl group are not polarised, if an electronegative group like chloro, carbonyl, nitro or cyano (in order to increase electronengativity) is attached to it, the $C-H$ bond gets polarised due to the inductive effect and the hydrogen atom becomes slightly acidic resulting in the formation of weak hydrogen bonds.

Though a weak bond, the H-bond effect a large number of the physical properties of compounds some of which are:

- Boiling point of liquids.
- Solubility of polar compounds in polar solvents (containing H attached with strong electronegative atom).
- Viscosity of liquids.
- Acidity

53. Which of the following combination can involve hydrogen bonding?

I. Mixture of KF and HF. **II.** Mixture of CH_3COCH_3 and $CHCl_3$

III. Mixture of NH_4Cl and H_2O **IV.** Mixture of CH_3OCH_3 and H_2O

(A) (I), (II) and (IV) **(B)** (I) and (II)

(C) (I), (II) and (III) **(D)** (I), (II), (III) and (IV)

54. For which of the following intramolecular H-bonding is not responsible?

(A) High value of pKa_2 for maleate acid ion $\begin{pmatrix} CHCOO^- \\ \| \\ CHCOOH \end{pmatrix}$ as compared to fumarate ion $\begin{pmatrix} CHCOO^- \\ \| \\ CHCOOH \end{pmatrix}$

(B) High viscosity of H_3PO_4 compared with $(CH_3)_3PO_4$

(C) High volatility of ortho-nitrophenol compared with para-isomer

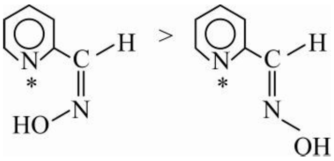
(D) Stability of chloral hydrate $[CCl_3CH(OH)_2]$ compared with $CH_3CH(OH)_2$

55. Which of the following is incorrectly matched?

(A) $H_2O > HF$ - (Enthalpy of vaporistaion)

(B) $SbH_3 > NH_3 > AsH_3 > PH_3$ - (Boiling point)

(C) $CH_2OHCHOHCH_2OH > CH_2OHCH_2OH$ - (Viscosity)

(D) 

- (Basicity of starred nitrogen)

Paragraph for Questions 56 - 58

Boiling point of covalent compound depends on intermolecular force. Intermolecular forces are the force of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electronic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds.

56. Which of the following hydrogen bond is the strongest?

(A) O – H- - - -N **(B)** F – H- - - -F **(C)** O – H- - - - O **(D)** O – H- - - - F

57. Liquidation of which gaseous substance will arise as a result of momentary imbalance in electronic distribution?

(A) Ammonia$_{(g)}$ **(B)** Carbon monoxide$_{(g)}$ **(C)** $Na^{+}_{(g)}\ Cl^{-}_{(g)}$ **(D)** Xenon$_{(g)}$

58. In which triad, first one has the highest boiling point?

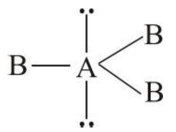
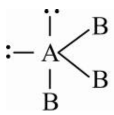
(A) PH_3, AsH_3, SbH_3 **(B)** HBr, HCl, HF

(C) $CH_3-O-CH_3, CH_3-S-CH_3, CH_3-Se-CH_3$ **(D)** AlF_3, SiF_4, PF_5

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labelled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

59. **MATCH THE FOLLOWING :**

	Column 1		Column 2
(A)	**Statement-1 :** In BCl_3, all Cl atoms are in same plane of B but in PCl_3 all Cl atoms are not in the plane of P. **Statement-2 :** In BCl_3, all Cl atoms are on corner of triangular plane but in PCl_3 all Cl atoms are on the base of the pyramid.	**(p)**	Statement-1 is correct.
(B)	**Statement-1 :** H_3PO_3 and H_3BO_3 increase H^+ ions concentration in water by different way. **Statement-2 :** In H_3PO_3 two hydrogens ionize in water but by H_3BO_3 only one hydrogen is lost in water.	**(q)**	Statement-2 is correct.
(C)	**Statement-1 :** AB_3E_2 type molecules have  type of arrangement rather than  (E = lone pair) **Statement-2 :** Structure have maximum symmetry and least valence shell electron pair repulsions out of all the hypothetical possibilities.	**(r)**	Statement-2 is correct explanation of Statement-1.
(D)	**Statement-1 :** In $H_2C=C=O$ (ketene) all the π- electrons are in same plane but in $H_2C=C=CH_2$ (allene) all π- electrons are not in same plane. **Statement-2 :** $H_2C=C=O$ is planar but $H_2C=C=CH_2$ is non-planar.	**(s)**	Statement-2 is incorrect.
		(t)	Statement-1 is incorrect

60. MATCH THE FOLLOWING :

	Column 1		Column 2
(A)	CsCl, CsBr, CsI	(p)	Increasing order of covalent character
(B)	LiOH, NaOH, KOH	(q)	Decreasing order of thermal stability
(C)	LiH, NaH, KH	(r)	Decreasing order of lattice energy
(D)	Mg_3N_2, Ca_3N_2, Sr_3N_2	(s)	Increasing order of thermal stability
		(t)	Increasing order of ionic character

61. MATCH THE FOLLOWING :

	Column 1		Column 2
(A)	Only $p\pi - p\pi$ bond is present	(p)	S_3O_9
(B)	Only $p\pi - d\pi$ bond is present	(q)	$H_3P_3O_9$
(C)	Both $p\pi - d\pi$ and $p\pi - p\pi$ bonds are present	(r)	SO_3
(D)	$X - O - X$ bond is present	(s)	CO_3^{2-}
		(t)	P_4O_{10}

62. MATCH THE FOLLOWING :

	Column 1		Column 2
(A)	CN	(p)	B.O. of corresponding cation ≥ 2
(B)	N_2	(q)	B.O. increasing when converted to corresponding (monopositive) cation
(C)	O_2	(r)	B.O. decreases when converted to corresponding anion (mononegative)
(D)	NO	(s)	Paramagnetic in both cationic (monopositive) as well as anionic (mononegative) form

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

63. Out of given ten molecules total molecules which have dipole moment zero is :

IOF_5, H_2O_2, ClF_3, CO_2, SO_2, P_4 S_8, $CH_2(CN)_2$, $C_2(CN)_4$, C_2N_2

64. In the following nine series select total number of series in which IInd member has high boiling point as compared to Ist member.

Series – CH_4, SiH_4, SnH_4
Series – NH_3, PH_3, AsH_3, SbH_3
Series – HF, HCl, HBr, HI
Series – He, Ne, Ar, Kr
Series – F_2, Cl_2 Br_2, I_2
Series – H_2O, H_2S, H_2Se, H_2Te
Series – BF_3, BCl_3, BBr_3
Series – o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene
Series – o-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde

65. For the given species number of species which do/does not exist :

BF_6^{3-}, BiCl, SH_2, HN_3, SI_6, $CsXeF_5$, PbI_2, ClF_7, NF_6^-, Li_2CO_3, KH_3

66. Out of given 9 statements total number of statements which are correct for graphite.

Statement – Three dimenstional network like structure.
Statement – C is sp^2 hybridised
Statement – Lubricant use
Statement - π - bond(s) present
Statement –C – C bond length is almost same as C_2H_6
Statement – van der waals forces present
Statement – Used as a abrasive
Statement – C – C bond length is more than $H-C\equiv C-H$
Statement – It conducts electricity.

67. Total number of water molecule(s) consumed for complete hydrolysis of one molecule of P_4O_{10} is:

68. Total number of oxygen atom(s) which act as bridge between any two silicon atom in mineral with composition MM'Si_3O_x (M = divalent metal ion and M' = tetravalent metal ion).

69. Find the number of molecules or ions in which d-orbitals is(are) not used in hybridisation.

PCl_6^-, PCl_4^+, IF_4^-, IF_5, XeO_3F_2, ICl_2^+, SF_2, SF_6, AsF_4^+, SiF_4

70. Find the total number of non-linear species out of given species :

I_3^-, $BeCl_2$, NH_2^-, OH_2, XeF_2, N_2O, SO_2, SF_2

71. Total number of molecules in which all the possible bond angles are identical :

PF_3, CF_4, XeF_4, PF_5, IF_7, BeF_2, SF_6

72. How many comparison(s) are INCORRECT among given ?

(i) H > Li (ionization energy)
(ii) Li > Be (size)
(iii) Na > Rb (size)
(iv) O > N (size)
(v) S > P (ionisation energy)
(vi) C > O (size)
(vii) B > Al (size)
(viii) F > Cl (ionization energy)
(ix) N > O (ionization energy)

73. Observed dipole moment of LiF is $6.32\,D$. Calculate percentage ionic character of LiF if bond length $(Li-F)$ is $0.156\,nm$.

74. P_4 is stable form of phosphorus. The percentage of p-character in the orbital forming $(P-P)$ bond in P_4 is :

75. At 300K and 1.00 atm, density of gaseous HF is $3.17\,gL^{-1}$. How many HF molecules are associated by H-bonding ?

[Given : $R = 0.0821\,L\,atm\,mol^{-1}\,K^{-1}$, Atomic mass of $H = 1$, $F = 9$]

76. A total of $n\times10^{20}$ energy levels are present in $3s$ conduction band of single crystal of sodium weighing $26.8\,mg$. What is the value of n ?

Advanced Problem Package	Chemical Equilibrium

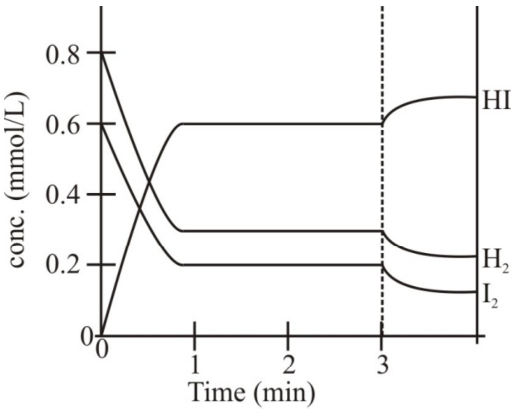
SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. At a certain temperature the equilibrium constant K_c is 0.25 for the reaction : $A_2(g) + B_2(g) \rightleftharpoons C_2(g) + D_2(g)$
If we take 1 mole of each of the four gases in a 10 litre container, what would be equilibrium concentration of $A_2(g)$.

(A) 0.12 **(B)** 0.13 **(C)** 0.14 **(D)** 0.15

2. The equation for the reaction in the figure below is : $H_2(g) + I_2(g) + \text{Heat} \rightleftharpoons 2HI(g)$.



At the instant 3 min, what change was imposed into the equilibrium?

(A) Pressure was increased **(B)** Temperature was increased
(C) Iodine was added to the system **(D)** Hydrogen was added to the system

3. A flask containing 0.5 atm of $A_2(g)$ contains some solid AB which undergoes dissociation according to

$$2AB(s) \rightleftharpoons A_2(g) + B_2(g).\ K_p = 0.06\ atm^2$$

Calculate the total pressure (in atm) at equilibrium :

(A) 0.70 atm **(B)** 0.80 atm **(C)** 0.90 atm **(D)** 1.0 atm

4. If for $2A_2B(g) \rightleftharpoons 2A_2(g) + B_2(g)$, $K_p =$ total pressure (at equilibrium) and starting the dissociation from 4 moles of A_2B, then :

(A) degree of dissociation of A_2B will be (2/3)
(B) total number of moles at equilibrium will be (14/3)
(C) at equilibrium the number of moles of A_2B are not equal to the number of moles of B_2
(D) at equilibrium the number of moles of A_2B are equal to the number of moles of A_2

5. 0.96 gm of HI was heated at 720 K till the equilibrium. The % dissociation of HI was found to be 21%. The volume and concentration of hypo required for the liberated I_2 is :

(A) 10 ml of 0.1 N $Na_2S_2O_3$
(B) 20 ml of 0.02 N $Na_2S_2O_3$
(C) 6 ml of 0.3 M $Na_2S_2O_3$
(D) None of these

6. The reaction $X_2 + Y_2 \rightleftharpoons 2XY$ was studied at a certain temperature. In the beginning 1.0 mole of X_2 was taken in a one litre flask and 2 moles of Y_2 was taken in another 2 L flask and both these containers are connected so equilibrium can be established. What is the equilibrium concentration of X_2 and Y_2? Given equilibrium concentration of [XY] = 0.6 mol/L.

(A) $\left(\frac{1}{3}-0.3\right),\left(\frac{2}{3}-0.3\right)$ **(B)** $\left(\frac{1}{3}-0.6\right),\left(\frac{2}{3}-0.6\right)$

(C) $(1-0.3),(2-0.3)$ **(D)** $(1-0.6),(2-0.6)$

7. Ammonia under a pressure of 15 atm at 27°C is heated to 347°C in a closed vessel in the presence of catalyst. Under these conditions, NH_3 partially decomposes to H_2 and N_2. The vessel is such that the volume remains effectively constant, whereas the pressure increases to 50 atm. Calculat the % of NH_3 actually decomposed at 347°C.

(A) 61.29% **(B)** 60.29% **(C)** 58.28% **(D)** 55.25%

8. Consider the reaction : $2NO_2(g) \rightleftharpoons N_2O_4(g)$ at 20°C.

If $\Delta G° = -5.39$ kJ and $K_p = 8.81$ for the reaction at 20°C, calculate the value of ΔG for the reaction when the partial pressures of NO_2 and N_2O_4 are 1.50 atm and 2.40 atm, respectively.

(A) –5.22 kJ **(B)** +4.71 kJ **(C)** –9.28 kJ **(D)** +154 kJ

9. PCl_5 dissociates into PCl_3 and Cl_2 : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The total pressure of the system is P at a density ρ and temperature T. If the vapour density of the gas mixture at equilibrium has the value of 62 when the temperature is 230ºC, what is the value of P/ρ.

(A) 0.3327 atm/gm/*l* **(B)** 33.27 atm/gm/*l* **(C)** 3.327 atm/gm/*l* **(D)** None of these

10. For the reaction : $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$; $K_p = 7.5$ at some temperature. If $p_{CO} = 0.100$ atm, $p_{Cl_2} = 0.200$ atm, and $P_{COCl_2} = 0.250$ atm, which of the following statements is true?

(A) The reaction is at equilibrium **(B)** At equilibrium, $p_{COCl_2} > 0.250$ atm

(C) At equilibrium, $p_{COCl_2} < 0.250$ atm **(D)** At equilibrium, $p_{CO} = p_{Cl_2}$

11. Hydrogen peroxide (H_2O_2) decomposes according to the equation : $2H_2O_2\ (\ell) \rightleftharpoons 2H_2O\ (\ell) + O_2(g)$

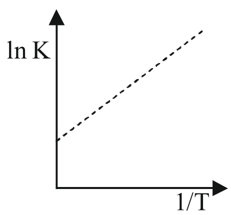
From the following data at 25°C, calculate the value of K_p at 400 K for the above reaction, $\Delta H° = -196.0$ kJ $\Delta S° = 125.65$ J/K.

(A) 1.44×10^{32} **(B)** 1.44×10^{-32} **(C)** 1.44×10^{3} **(D)** 1.3×10^{15}

12. What is the slope of the following line?

(A) $\frac{1}{T \ln K}$ **(B)** $\frac{T\Delta S°}{R}$

(C) $\frac{-\Delta H°}{R}$ **(D)** $\frac{\ln K}{T}$



13. The reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ is in equilibrium in a 1.0 L flask, and has 0.20 mol of A, 0.20 mole of B, 0.40 mole of C, and 0.40 mole of D. If 0.15 mole of A and 0.15 mole of B are then added to the system at equilibrium, what will be the concentration of A once a new equilibrium point is reached?

(A) 0.050 M **(B)** 0.10 M **(C)** 0.20 M **(D)** 0.25 M

14. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; if percentage dissociation of N_2O_4 varies as 25%, 50%, 75% and 100%, then the corresponding observed vapour densities of the reaction mixture are related as :

(A) $d_1 > d_2 > d_3 > d_4$ **(B)** $d_4 = d_3 > d_2 > d_1$ **(C)** $d_1 = d_2 = d_3 = d_4$ **(D)** $(d_1 = d_2) > (d_3 = d_4)$

15. 40% of a mixture of 0.2 mole of N_2 and 0.6 mole of H_2 react to give NH_3 according to the equation $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at given temperature and pressure. Then the ratio of the final volume to the initial volumes of gases are as :

(A) 4:5 **(B)** 5:4 **(C)** 7:10 **(D)** 8:5

16. The K_p for the reaction $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ is 640mm Hg at 775K. At what pressure the dissociation will be 50 % : [Give answer in mm Hg]

(A) 460 **(B)** 470 **(C)** 480 **(D)** 490

17. N_2O_4 dissociates as $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At 50°C and 1 atm pressure, N_2O_4 dissociates 40%. The pressure at which mole ratio of $N_2O_4 : NO_2$ is 1 : 8, at same temperature is :

(A) 0.107 atm **(B)** 0.15 atm **(C)** 0.63 atm **(D)** 0.3 atm

18. N_2O_3 on decomposition gives NO and NO_2, they are found to be in equilibrium at 300 K. If the vapour density of such an equilibrium mixture is 23.75, then calculate percentage by mass of N_2O_3 in the equilibrium mixture?

(A) 80 % **(B)** 60 % **(C)** 40 % **(D)** 20 %

19. The pH of blood is maintained by the balance between H_2CO_3 and $NaHCO_3$. If the amount of CO_2 in the blood is increased, how will it effect the pH of blood ?

(A) pH will increase **(B)** pH will decrease **(C)** pH will be 7 **(D)** pH will remain same at 7.4

Paragraph for Questions 20 - 21

Effect of temperature on the equilibrium process is analyzed by using the thermodynamics. From the thermodynamic relation

$\Delta G° = -2.303 RT \log K$ … (i) $\Delta G°$: Standard free energy change

$\Delta G° = \Delta H° - T\Delta S°$ … (ii) $\Delta H°$: Standard heat of the reaction

From (i) and (ii)

$-2.303RT \log K = \Delta H° - T\Delta S°$ $\Delta S°$: Standard entropy change

$$\Rightarrow \quad \log K = -\frac{\Delta H°}{2.303RT} + \frac{\Delta S°}{2.303R} \quad \ldots \text{(iii)}$$

If a plot of log K vs 1/T is made, then it is a straight line having slope $= \frac{-\Delta H°}{2.303R}$ and Y intercept $= \frac{\Delta S°}{2.303R}$

If at temperature T_1, equilibrium constant be K_1 and at temperature T_2, equilibrium constant be K_2 then the above equation reduces to :

$$\Rightarrow \quad \log K_1 = -\frac{\Delta H°}{2.303RT_1} + \frac{\Delta S°}{2.303R} \quad \ldots \text{(iv)}$$

$$\Rightarrow \quad \log K_2 = -\frac{\Delta H°}{2.303RT_2} + \frac{\Delta S°}{2.303R} \quad \ldots \text{(v)}$$

Subtracting (iv) from (v) we get, $\log\frac{K_2}{K_1} = \frac{\Delta H°}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

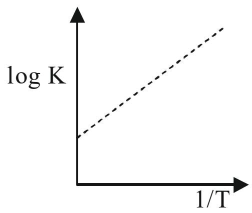
From the above relation we can conclude that the value of equilibrium constant increases with increase in temperature for an endothermic reaction and the same decreases with the increase in temperature of an exothermic reaction. Answer the following three questions based on the above information.

Read the paragraph carefully and answer the following questions:

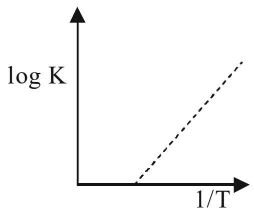
20. If standard heat of dissociation of PCl_5 is 230 cal, then slope of the graph of $\log K$ vs 1/T is :

(A) +50 **(B)** –50 **(C)** 10 **(D)** None of these

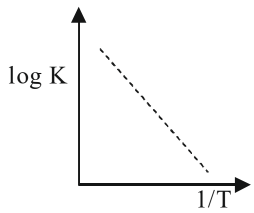
21. For exothermic reaction if 0, then the sketch of log K vs 1/T may be :



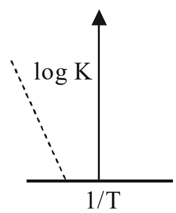
(A)



(B)



(C)



(D)

22. If for a particular reversible reaction : $K_c = 57$ at 355°C and $K_c = 69$ at 450°C, then :

(A) $\Delta H < 0$ **(B)** $\Delta H > 0$ **(C)** $\Delta H = 0$

(D) Sing of ΔH can't be determined

Paragraph for Questions 23 - 25

Paragraph : Two containers A and B of capacity 1 litre and 2 litre respectively is connected by tube of negligible volume. The tube is initially closed by stopcock and 'A' contains small amount of $H_2O(l)$ and B contain initially pure $COCl_2(g)$ at pressure of 100 torr. The gas $COCl_2$ partially dissociates at experimental condition into CO(g) and $Cl_2(g)$.

Now the stopcock connecting two container is opened and sufficient time is given to attain final equilibrium. The final pressure at equilibrium is found to be 100 torr in both containers.

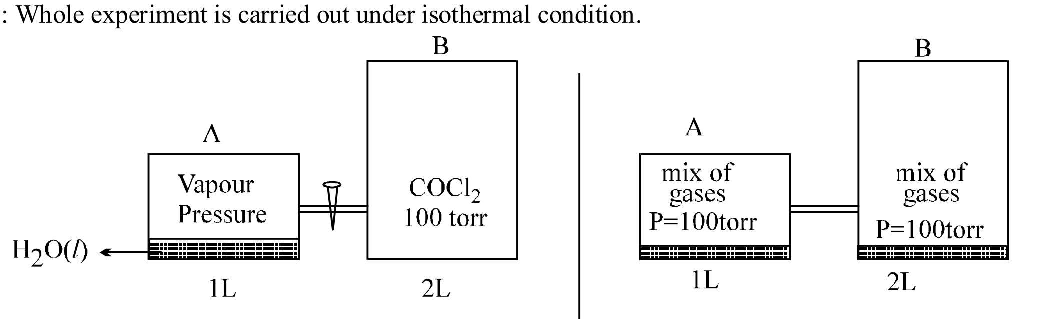
Using given data and taking following assumption calculate the mole fraction of CO(g) in final state.

Given : Vapour pressure of H_2O at experimental temperature 'T' is equal to 20 torr.

Assumption-1 : Volume of $H_2O(l)$ is small and can be neglected but sufficient to create vapour pressure in both container.

Assumption-2 : $COCl_2$, CO and Cl_2 gas do not dissolve in $H_2O(l)$.

Assumption-3 : Whole experiment is carried out under isothermal condition.



'Initial state' at temp. 'T'

Final state at temp. 'T'

23. Pressure of $COCl_2(g)$ in the gaseous mixture in final state :

(A) 80 **(B)** 80/3 **(C)** 160/3 **(D)** 40/3

24. The ratio of number of moles of CO(g) to total number of moles of gases in the final state.

(A) 4/15 **(B)** 8/15 **(C)** 6/15 **(D)** 2/15

25. Ratio of the partial pressure of CO(g) and $COCl_2(g)$ in final state :

(A) 5 : 1 **(B)** 4 : 1 **(C)** 1 : 4 **(D)** 1 : 5

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

26. Consider the following reversible systems

$$N_2 + O_2 \xrightleftharpoons{K_1} 2NO \; ; \; \frac{1}{2}N_2 + \frac{1}{2}O_2 \xrightleftharpoons{K_2} NO \; ; \; 2NO \xrightleftharpoons{K_3} N_2 + O_2;$$

$$NO \xrightleftharpoons{K_4} \frac{1}{2}N_2 + \frac{1}{2}O_2;$$

Correct relation between K_1, K_2, K_3 and K_4 is :

(A) $K_1 \times K_3 = 1$ **(B)** $\sqrt{K_1} \times K_4 = 1$

(C) $\sqrt{K_3} \times K_2 = 1$ **(D)** None of these

27. Which of the following is/are correct for the reaction with equilibrium constant K?

$$A(g) + B(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C(g) + D(g) \; ; \; \Delta H = 20 \text{ J}$$

(A) K_{eq} will increase on increasing temperature
(B) k_f will increase on increasing temperature
(C) k_b will increase on increasing temperature
(D) k_b will decrease on increasing temperature

28. For the equilibrium reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta G° = -30$ kJ

In which of the following case, the reaction will move (spontaneous) in forward direction to achieve equilibrium? (Given: 2.303 RT = 5.705 kJ) (log 1.8 = 0.25).

(A) $p_{N_2} = 1$ atm, $p_{H_2} = 1$ atm and $p_{NH_3} = 1$ atm at 298 K.
(B) $p_{N_2} = 10$ atm, $p_{H_2} = 10$ atm and $p_{NH_3} = 0.01$ atm at 298 K.
(C) $p_{N_2} = 1$ atm, $p_{H_2} = 1$ atm and $p_{NH_3} = 0.001$ atm at 298 K.
(D) $p_{N_2} = 0.01$ atm, $p_{H_2} = 0.001$ atm and $p_{NH_3} = 0.01$ atm at 298 K.

29. Ammonia is manufactured by reaction of N_2 and H_2 by Haber's process. An equilibrium mixture obtained by mixing H_2 & N_2 contains 3.4 gm each of N_2, H_2 & NH_3.

Select the correct option(s).

(A) Mass of N_2 present initially was 6.2 gm
(B) Mass of H_2 present initially was 4 gm
(C) Maximum amount of NH_3 that can be produced is 22.66 gm if N_2 & H_2 reacts completely
(D) None of these

30. For which of the following reaction, does value of equilibrium constant independent of choice of standard state.

(A) $CO(g) + H_2O\ (g) \rightarrow CO_2(g) + H_2(g)$ **(B)** $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$

(C) $NO(g) \rightarrow 1/2N_2\ (g) + 1/2O_2(g)$ **(D)** $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

31. What is general criteria of choosing a suitable indicator for a given titration ?

(A) The indicator should have a broad pH range
(B) pH at the end point of titration should be close to neutral point of indicator
(C) Indicator should have neutral point at pH = 7
(D) The indicator must show a sharp colour change near the equivalence point of titration point

32. When $AgNO_3$ is heated mildly in a closed vessel, oxygen is liberated and $AgNO_2$ is left behind. At equilibrium according to reaction $AgNO_3(s) \rightleftharpoons AgNO_2(s) + \frac{1}{2}O_2(g)$:

(A) Addition of $AgNO_2$ favours reverse reaction
(B) Addition of $AgNO_3$ favours forward reaction
(C) Increasing temperature favours forward reaction
(D) Increasing pressure favours reverse reaction

33. 1 mole each of $N_2(g)$ and $O_2(g)$ are introduced in a 1L evacuated vessel at 523 K and equilibrium concentrations:

(A) Change on changing pressure
(B) Change on changing temperature
(C) Change on changing volume of the vessel
(D) Remain same even when a platinum gauze is introduced to catalyse the reaction

34. For the reaction, $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

If pressure is increased by reducing the volume of the container, then :

(A) Total pressure at equilibrium will change
(B) Concentration of all the components at equilibrium change
(C) Concentration of all the components at equilibrium will remain same
(D) Equilibrium will shift in the forward direction

35. Which of the following is/are correct about the influence of positive catalyst on a chemical equilibrium ?

(A) Equilibrium constant is unaffected
(B) Heat of reaction ΔH is unaffected
(C) Amount of product remains unaffected
(D) Larger amount of product is formed

36. An increase in temperature increase which of the following?

1. The rate constant of a reaction
2. The ionic product of water
3. The equilibrium constant of exothermic reactions

(A) 1 and 2 only **(B)** 1 and 3 only
(C) 2 and 3 only **(D)** 1, 2 and 3

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labelled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

37. **MATCH THE FOLLOWING:**

	Column 1		Column 2
(A)	For the equilibrium $NH_4I(s) \rightleftharpoons NH_3(g)+HI(g)$, if pressure is increased at equilibrium	**(p)**	Forward shift
(B)	For the reaction : $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium, volume is increased at equilibrium	**(q)**	No change
(C)	For the reaction : $H_2O(g)+CO(g) \rightleftharpoons H_2(g)+CO_2(g)$ inert gas is added at constant pressure at equilibrium.	**(r)**	Backward shift
(D)	For the equilibrium : $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$, Cl_2 is removed at equilibrium	**(s)**	Final pressure is more than initial pressure

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

38. Consider the following reversible reaction : $NO(g)+NO_3(g) \rightleftharpoons 2NO_2(g)$
If 1.0 mol of NO is mixed with 3.0 mol of NO_3, 'x' mol of NO_2 is produced at equilibrium. If 2.0 mol of NO is added further, 'x' mol of NO_2 is further produced. What is the value of equilibrium constant?

39. Consider the following reversible reactions :

$$A+B \rightleftharpoons P \quad ; \quad K_c = 6$$

$$2B+C \rightleftharpoons 2D \quad ; \quad K_c = 4$$

Hence, equilibrium constant (K_c) for the reaction $A+D \rightleftharpoons P+\frac{C}{2}$ is ________ .

40. For a reversible reaction $A \rightleftharpoons P$, the equilibrium constant is expressed as : $\log K = 0.47 - \frac{2000}{T}$ (All values in SI unit) the standard entropy of reaction $\left(\Delta S^\circ_{rxn}\right)$ is closest to which integer (in) JK^{-1} unit)?

41. An equilibrium mixture containing both NO_2 and N_2O_4 at 2.0 atm is expanded at constant temperature till the equilibrium partial pressure of N_2O_4 decreases to 0.85 atm. By what factor the volume of equilibrium mixture were increased? (Approximate the answer to the nearest integer).

42. An equilibrium mixture contain equal moles (n) of each PCl_5, PCl_3 and Cl_2. If $\frac{20}{3}$ mol of $Cl_2(g)$ is added to equilibrium at constant temperature and pressure, volume of the system is doubled. What is approximate value of n?

43. Consider the following reversible system : $A(g)+2B(g) \rightleftharpoons AB_2(g);\ K_c = \frac{1}{2}$
The above equilibrium is established in a 1.0 L flask and at equilibrium 2 moles of each A and B are present. If 2.0 moles of B is added further, how many moles of AB_2 should be added so that moles of A does not change?

44. If for the reversible reaction $A \rightleftharpoons P$, $\Delta G^\circ = 0$. Therefore, the value of equilibrium constant is

45. A reaction, $A(g) + 2B(g) \rightleftharpoons 2C(g) + D(g)$ was studied using an initial concentration of B which was 1.5 times that of A. But the equilibrium concentrations of A and B were found to be equal. The value of K_p for the equilibrium is

46. For the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$ equilibrium pressure was found to be 3 atm at 1000 K, hence K_p in atm^3 is _________.

47. In the following reaction at equilibrium,

$$A(l) + B(g) \rightleftharpoons C(g) + D(g)$$

it was observed that vapour pressure of A is 2 atm and the pressure exerted by B, C and D are 1 atm, 2 atm and 3 atm respectively. What is the value of K_p?

48. In a basic aqueous solution chloromethane undergoes a substitution reaction in which Cl^- is replaced by OH^- as

$$CH_3Cl(aq) + OH^- \rightleftharpoons CH_3OH(aq) + Cl^-(aq)$$

The equilibrium constant of above reaction $K_c = 1 \times 10^{16}$. If a solution is prepared by mixing equal volumes of 0.1 M CH_3Cl and 0.2 M NaOH (100% dissociated) then $[OH^-]$ concentration at equilibrium in mixture will be________M.

49. 10 lt box contain O_3 and O_2 at equilibrium at 2000 K. The $\Delta G^\circ = -534.52$ kJ at 8 atm equilibrium pressure. The following equilibrium is present in the container $2O_3(g) \rightleftharpoons 3O_2(g)$. The partial pressure of O_3 is $x \times 10^{-7}$ atm. The numerical value of x is________. ($\ln 10 = 2.3$, $R = 8.3\ J\ mole^{-1}K^{-}$)

50. For the equilibrium, $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ the value of K_p is $0.109\ atm^2$ at 300 K. The vapour pressure of NH_4HS at 300 K in atm would be________.

51. The average person can see the red colour imparted by the complex $[Fe(SCN)]^{2+}$ to an aqueous solution if the concentration of the complex is 6×10^{-6} M or greater. What minimum concentration of KSCN would be required to make it possible to detect 1 ppm (part per million) of Fe (III) in a natural water sample ?

The instability constant for $Fe(SCN)^{2+} \rightleftharpoons Fe^{3+} + SCN^-$ is 7.142×10^{-3}. [Given : Atomic mass Fe = 56]

52. Following two equilibria are established on mixing two gases A_2 and C.

(i) $3A_2(g) \rightleftharpoons A_6(g)$ $\quad K_p = 1.6\ atm^{-2}$

(ii) $A_2(g) + C(g) \rightleftharpoons A_2C(g)$

If A_2 and C are mixed in 2 : 1 molar ratio, calculate the K_p for the reaction (ii). Given that the total pressure to be 1.4 atm and partial pressure of A_6 to be 0.2 atm at equilibrium.

53. When equal volumes of 0.2 M $AgNO_3$ and 1 M KCN solutions were mixed then at equilibrium, concentration of Ag^+ was found to be 10^{-6} M. While when equal volumes of 0.2 M $Zn(NO_3)_2$ solution and of 1 M KCN solution were mixed then at equilibrium, concentration of Zn^{2+} ion was found to be 10^{-12} M. The equilibrium constant of reaction $2[Ag(CN)_2]^- + Zn^{2+} \rightleftharpoons [Zn(CN)_4]^{2-} + 2Ag^+$ is $x \times 10^{21}$. The numerical value of x is________.

Advanced Problem Package	Ionic Equilibrium

SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. The pH of a solution obtained by mixing equal volume of solutions having pH = 3 and pH = 4. [log 5.5 = 0.7404]
(A) 3.38 **(B)** 3.5 **(C)** 3.26 **(D)** 4.0

2. 50 mL of 0.1M of H_3CCOOH is titrated against 0.1M NaOH solution. What will be the pH of the solution when 25 mL of NaOH is added? [Given: K_a of $H_3C–COOH = 2 \times 10^{-5}$; log 2 = 0.3]
(A) 3.50 **(B)** 7.00 **(C)** 4.70 **(D)** 5.30

3. The pH values of 1 M solutions of CH_3COOH (I), CH_3COONa (II), CH_3COONH_4 (III) and KOH (IV) will be in the order
(A) IV > III > II > I **(B)** IV > II > III > I **(C)** I > III > II > IV **(D)** II > I > III > IV

4. Carbonic acid, H_2CO_3, is a diprotic acid for which $K_1 = 10^{-7}$ and $K_2 = 10^{-11}$. Which solution will produce a pH closest to 9?
(A) 0.1 M H_2CO_3 **(B)** 0.1 M Na_2CO_3
(C) 0.1 M $NaHCO_3$ **(D)** 0.1 M $NaHCO_3$ and 0.1 M Na_2CO_3

5. The ratio of degree of ionization of the two monobasic acids is 1 : 10 and the ratio of their ionization constants is 1 : 50. What would be the ratio of their concentrations?
(A) 1 : 2 **(B)** 2 : 1 **(C)** 1 : 1 **(D)** none of these

6. The solubility of $PbCl_2$ in water is 0.01 M at 25°C. The maximum concentration of Pb^{2+} in 0.1 M NaCl will be :
(A) 2×10^{-3} M **(B)** 1×10^{-4} M **(C)** 1.6×10^{-2} M **(D)** 4×10^{-4} M

7. The solubility of a saturated solution of calcium fluoride is 2×10^{-4} moles per litre. Its solubility product is :
(A) 32×10^{-10} **(B)** 32×10^{-8} **(C)** 32×10^{-14} **(D)** 32×10^{-12}

8. The ratio of dissociation constants of two weak acids HA and HB is 4. At what molar concentration ratio, the two acids will have same pH?
(A) 2 **(B)** 0.5 **(C)** 4 **(D)** 0.25

9. What will be the pH of a solution formed by mixing 40 cm^3 of 0.1 M HCl with 10 cm^3 of 0.45 M NaOH?
(A) 10 **(B)** 8 **(C)** 5 **(D)** 12

10. When 0.22 mole of CH_3NH_2 (ionization constant, $K_b = 10^{-6}$) is mixed with 0.02 mole HCl and the volume is made up to 1 litre, find the $[H^+]$ of resulting solution at 25ºC.
(A) 10^{-5} M **(B)** 2×10^{-9} M **(C)** 2×10^{-5} M **(D)** 10^{-9} M

11. Which is the correct representation for the solubility product constant of Ag_2CrO_4 ?
(A) $[Ag^+]^2[CrO_4^{2-}]$ **(B)** $[Ag^+]\ [CrO_4^{2-}]$ **(C)** $[2Ag^+]\ [CrO_4^{2-}]$ **(D)** $[2Ag^+]^2[CrO_4^{2-}]$

12. Which of the following solution acts as a buffer?
(A) HCl + NaCl **(B)** NaOH + NaCl **(C)** $CH_3COOH + CH_3COONa$ **(D)** H_2SO_4 + NaOH

13. Buffer solution is prepared by mixing 10 ml of 1.0 M acetic acid and 20 ml of 0.5 M sodium acetate and then diluted to 100 ml with distilled water. If the pK_a of CH_3COOH is 4.76, what is the pH of the buffer solution prepared?
(A) 5.21 **(B)** 4.76 **(C)** 4.34 **(D)** 5.21

14. The pK_b value of ammonium hydroxide is 4.75. An aqueous solution of ammonium hydroxide is titrated with HCl. The pH of the solution at the point where half of ammonium hydroxide has been neutralised will be :

(A) 9.25 **(B)** 8.25 **(C)** 7.50 **(D)** 4.75

15. The solubility product of AgI at 25°C is 1.0×10^{-16} $mol^2\ L^{-2}$. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately : (in mol L^{-1})

(A) 1.0×10^{-12} **(B)** 1.0×10^{-10} **(C)** 1.0×10^{-8} **(D)** 1.0×10^{-16}

16. The self–ionisation constant of NH_3 at 50°C is given by $K_{NH_3} = [NH_4^+]\ [NH_2^-] = 10^{-30}$. How many NH_2^- ions are present per cm^3 of pure liquid NH_3? (Assume Avogadro's number = 6×10^{23})

(A) 6×10^6 **(B)** 6×10^5 **(C)** 6×10^{-5} **(D)** 6×10^{-6}

17. A buffer solution is to be made by using conjugate acid–base pair. Which of the following pair will be most suitable for preparing a buffer solution having pH = 7.1? (given: log 2 = 0.3)

	Acid	Conjugate base	K_a
(A)	H_2CO_3	HCO_3^-	8×10^{-7}
(B)	NH_4^+	NH_3	8×10^{-10}
(C)	$C_5H_5NH^+$	C_5H_5N	8×10^{-6}
(D)	NaH_2PO_4	Na_2HPO_4	8×10^{-8}

18. At 25°C, the dissociation constants of CH_3COOH and NH_4OH in aqueous solution are almost the same i.e., 10^{-5}. If pH of some acetic acid solution is 3, the pH of NH_4OH solution of same concentration at the same temperature would be

(A) 3.0 **(B)** 4.0 **(C)** 10.0 **(D)** 11.0

19. The ionization constant of an acid-base indicator (a weak acid) is 1.0×10^{-6}. The ionized form of the indicator is red whereas the unionized form is blue. The pH change required to alter the colour of the indicator from 80% blue to 80% red is

(A) 2.00 **(B)** 1.40 **(C)** 1.20 **(D)** 0.80

Paragraph for Questions 20 - 22

The solubility product of a soluble salt A_xB_y is given by: $K_{sp} = [A^{y+}]^x\ [B^{x-}]^y$. As soon as the product of concentration of A^{y+} and B^{x-} becomes more than its K_{sp}, the salt begins to precipitate. It may practically be noticed that AgCl is fairly soluble in water and its solubility decreases dramatically in 0.1 M NaCl or 0.1 M $AgNO_3$ solution. It may, therefore, be concluded that in presence of a common ion, the solubility of salt decreases.

Read the paragraph carefully and answer the following questions:

20. K_{sp} of SrF_2 in water is 8×10^{-10}. The solubility of SrF_2 in 0.1 M NaF aqueous solution is

(A) 8×10^{-10} **(B)** 2×10^{-3}

(C) 2.7×10^{-10} **(D)** 8×10^{-8}

21. Equal volume of the following two solutions are mixed. The one in which $CaSO_4$ ($K_{sp} = 2.4 \times 10^{-5}$) is precipitated is :

(A) 0.02 M $CaCl_2$ + 0.0004 M Na_2SO_4 **(B)** 0.01 M $CaCl_2$ + 0.0004 M Na_2SO_4

(C) 0.02 M $CaCl_2$ + 0.0002 M Na_2SO_4 **(D)** 0.03 M $CaCl_2$ + 0.004 M Na_2SO_4

22. The pH of a saturated solution of $Mg(OH)_2$ is (K_{sp} $Mg(OH)_2 = 1 \times 10^{-11}$). $(\log 2.7 = 0.43)$

(A) 9 **(B)** 3.87 **(C)** 10.43 **(D)** 5

Paragraph for Questions 23 - 25

Acidity or alkalinity of a solution depend upon the concentration of hydrogen ion relative to that of hydroxyl ions. The product of hydrogen ion and hydroxyl ion concentration is given by $K_w = [H^+][OH^-]$.

The value of K_w depends only on the temperature and not on the individual ionic concentration. If the concentration of hydrogen ion exceeds that of the hydroxyl ions, the solution is said to be acidic; whereas, if concentration of hydroxyl ion exceeds that of the hydrogen ions, the solution is said to be alkaline. The pH corresponding to the acidic and alkaline solutions at 25°C will be less than and greater than seven, respectively. We can confirm the above facts by taking 0.5 M CH_3COOH is taken for the experiments. (Given : K_a of acetic acid = 1.8×10^{-5})

Read the paragraph carefully and answer the following questions :

23. Degree of dissociation of acetic acid is :

(A) 66×10^{-2} **(B)** 6×10^{-3}
(C) 3×10^{-3} **(D)** 5×10^{-3}

24. pH of the solution will be :

(A) 2.52 **(B)** 2.22
(C) 5.04 **(D)** 2

25. If pH of the solution is doubled, what will be the concentration of acetic acid : [antilog 0.96 = 9.12]

(A) 1.8×10^{-5} M **(B)** 1.0 M
(C) 1.37×10^{-5} M **(D)** 1.25×10^{-3} M

Paragraph for Questions 26 - 28

Acid-base indicators are either weak organic acids or weak organic bases. Indicator change colour in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colourless substance in any aqueous solution with a pH less than 8.3. In between the pH range 8.3 to 10, transition of colour (colourless to pink) takes place and if pH of solution is greater than 10 solution is dark pink. Considering an acid indicator HIn, the equilibrium involving it and it's conjugate base (In^-) can be represented as : $\underset{\text{acidic form}}{HIn} \rightleftharpoons H^+ + \underset{\text{basic form}}{In^-}$

pH of solution can be computed as : $pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$

In general, transition of colour takes place in between the pH range, $pK_{In} \pm 1$.

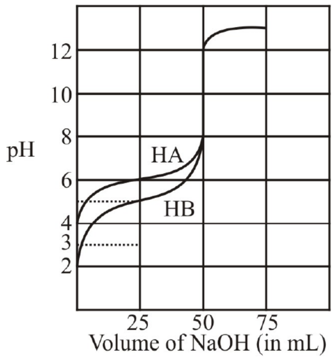
26. An indicator is a weak acid and pH range is 4.0 to 6.0. If indicator in 50% ionized in a given solution, then what is the ionization constant of the acid?

(A) 10^{-4} **(B)** 10^{-5}
(C) 10^{-6} **(D)** None of these

27. Select the correct statement(s) :

(A) At midway in the transition of an acidic indicator, $pH = pK_{In}$
(B) Methyl orange (3.1 to 4.4) is a suitable indicator for titration of weak acid and strong base
(C) Bromothymol blue (6.0 to 7.6) is not a good indicator for titration of HCl and NaOH
(D) Thymol blue (1.2 to 2.8) is a very good indicator for titration of 100 mL of 0.1 M NH_4OH (pK_b = 4.74) and 0.1 M HCl

28. Following is the titration curve of two acids HA and HB (5 milli-moles each) titrated against strong base NaOH(0.1 M)



What is pK_a for HB acid?

(A) 3 **(B)** 4 **(C)** 5 **(D)** 6

29. What is the equilibrium constant for the reaction : $HB(aq.) + NaA(aq.) \rightleftharpoons HA(aq.) + NaB(aq.)$?

(A) 10 **(B)** 0.1 **(C)** 10^{-7} **(D)** 10^{-11}

30. Calculate the pH at equivalent point when HB is titrated with NaOH.

(A) 8.75 **(B)** 8.85 **(C)** 9.0 **(D)** None of these

31. Which of the following indicator is most suitable for titration of HB with strong base :

(A) Phenolphthalein (8.3 – 10) **(B)** Bromothymol blue (6 – 7.6)

(C) Methyl red (4.2 – 6.3) **(D)** Malachite green (11.4 – 13)

Paragraph for Questions 32 - 35

In qualitative analysis, cations of group II as well as group IV both are precipitated as metal sulphides. Due to low value of Ksp of group II sulphides, Group reagent is H_2S in the presence of dil. HCl and due to high value of K_{sp} of group IV sulphides, Group reagent is H_2S in the presence of NH_4OH and NH_4Cl. In a solution containing 0.1 M each of Sn^{2+}, Cd^{2+} and Ni^{2+} ions, H_2S gas is passed…….

$$K_{sp} \text{ of } SnS = 8\times10^{-29},\ K_{sp} \text{ of } CdS = 1\times10^{-28},\ K_{sp} \text{ of } NiS = 3\times10^{-21},\ K_1 \text{ of } H_2S = 1\times10^{-7},\ K_2 \text{ of } H_2S = 1\times10^{-14}$$

32. If H_2S is passed into the above mixture in the presence of HCl, which ion will be precipitated first?

(A) SnS **(B)** CdS

(C) NiS **(D)** SnS and CdS (both together)

33. At what value of pH, NiS will start to precipitate (saturated solution of H_2S is 0.1 M ? (Given : $\log 5.77 = 0.76$)

(A) 12.76 **(B)** 7 **(C)** 1.24 **(D)** 4

34. Which of the following sulphide is more soluble in pure water?

(A) CdS **(B)** NiS **(C)** SnS **(D)** Equal solubility for all

35. If 0.1 M HCl is mixed in the solution containing only 0.1 M Cd^{2+} ions and saturated with H_2S, then $[Cd^{2+}]$ remaining in the solution after CdS stops to precipitate is :

(A) 10^{-8} **(B)** 8.2×10^{-9}

(C) 5.6×10^{-6} **(D)** 5.6×10^{-10}

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

36. Which of the following form conjugate acid-base pairs in the right order?

(A) NH_3, NH_2^- **(B)** OH^-, H_2O
(C) HCO_3^-, CO_3^{2-} **(D)** H_2S, HS^-

37. A weak acid HA has a pH = 4. Which of the following conditions satisfy the same?

(A) $C = 10^{-3}$, $\alpha = 10\%$ **(B)** $C = 10^{-2}$, $K_a = 10^{-6}$
(C) $[A^-] = 10^{-4}$ **(D)** $K_a = 10^{-2}$, $\alpha = 10\%$

38. Which among the following statements is(are) correct?

(A) pH of 10^{-8} M HCl is equal to 8
(B) Conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(C) pH of 0.1 M NaCl (aqueous solution) $= \frac{1}{2} pK_w$
(D) Ionization of water increases with decrease in temperature

39. In the following reaction:

$$\underset{(A)}{[Cu(H_2O)_3(OH)]^+} + \underset{(B)}{[Al(H_2O)_6]^{3+}} \rightarrow \underset{(C)}{[Cu(H_2O)_4]^{2+}} + \underset{(D)}{[Al(H_2O)_5(OH)]^{2+}}$$

(A) (A) is an acid and (B) is a base **(B)** (A) is a base and (B) is an acid
(C) (C) is the conjugate acid of (A) and (D) is the conjugate base of (B)
(D) (C) is the conjugate base of (A) and (D) is the conjugate acid of (B)

40. In which of the following pairs of solutions is there no effect on the pH upon dilution?

(A) 0.1 M NH_3 and 0.1 M $(NH_4)_2SO_4$ **(B)** 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4
(C) 0.1 M HCl and 0.01 M NaOH **(D)** 0.1 M KCl and 0.1 M HCl

41. Which of the following solution in water act as buffer?

(A) 0.1 mol of NaOH + 0.15 mol of CH_3COOH
(B) CH_3COONH_4
(C) 0.5 mol of pyridine + 0.5 mol of Pyridinium chloride
(D) 0.25 mol of NH_4Cl + 0.5 mol of NaOH

42. Pure AgCl(s) is added to (i) 0.01 M $AgNO_3$ solution (ii) 0.025 M KCl solution and both suspensions are shaken well. What is the approximate ratio of the $[Cl^-]$ in the first solution to the $[Ag^+]$ in the second solution?

(A) 2.5 **(B)** 2.0 **(C)** 3.0 **(D)** 1.5

43. If concentrations of two acids are same, their relative strengths can be compared by :

(A) α_1 / α_2 **(B)** K_1/K_2
(C) $[H^+]_1/[H^+]_2$ **(D)** $\sqrt{K_1 / K_2}$

44. Which can act as buffer?

(A) CH_3COOH + NaOH, if $[CH_3COOH] > [NaOH]$
(B) HCl + CH_3COONa, if $[CH_3COONa] > [HCl]$
(C) NH_4CN
(D) HCN + NaCN

45. Which is(are) wrong statement(s)?
(A) All Arrhenius acids are also Bronsted acid but all Arrhenius bases are not Bronsted bases
(B) All Bronsted bases are Lewis bases
(C) All Bronsted acids are Lewis acids
(D) Conjugate base of a strong acid is strong

46. Factor influencing the degree of dissociation of a weak electrolyte is :
(A) Dilution **(B)** Temperature **(C)** Presence of other ions **(D)** Nature of solvent

47. Dissociation of an indicator can be considered as $HIn \rightleftharpoons H^+ + In^-$. Colour of HIn is P and In^- is Q. Given that ratio of conc. of HIn to In^- rangers from 10 to 1/10, then which of the following statement is/are correct?
(A) Solution assumes P-colour, when $pH \le pK_{In} - 1$
(B) Solution assumes Q-colour, when $pH \ge pK_{In} + 1$
(C) Solution assumes P-colour, when $pH \ge pK_{In} + 1$
(D) Solution assumes Q-colour, when $pH \le pK_{In} - 1$

48. An acid indicator (HIn) has $K_a = 3 \times 10^{-5}$, the acid from is red and basic form is blue. Which is correct?
(A) pH = 5 when indicator is 75% red **(B)** pH = 4.05 when indicator is 75% red
(C) pH = 5 when indicator is 75% blue **(D)** pH = 4.05 when indicator is 75% blue

49. Which among the following statement is/are correct?
(A) $pH = -\log_{10}[H_3O^+]$
(B) pH of water decreases with increase of temperature
(C) pH cannot be zero, negative or more than 14
(D) If a solution is diluted ten times, its pH increases by 1

50. If concentrations of two weak acids are same, their relative strengths can be compared by :
(A) α_1/α_2 **(B)** K_1/K_2 **(C)** $[H^+]_1/[H^+]_2$ **(D)** $\sqrt{K_1/K_2}$

51. Which can act as buffer ?
(A) $CH_3COOH + NaOH$, if $[CH_3COOH] > [NaOH]$ **(B)** $HCl + CH_3COONa$, if $[CH_3COONa] > [HCl]$
(C) NH_4CN **(D)** $HCN + NaCN$

52. Which is/are wrong statement(s) ?
(A) Arrhenius acids are also Bronsted acid but not vice-versa
(B) All Bronsted bases are Lewis bases
(C) All Lewis acids are Bronsted acids
(D) Conjugate base of a strong acid is strong

53. Dissociation of an indicator can be considered as $Hln \rightleftharpoons H^+ + ln^-$. Colour of Hln is P and ln^- is Q. Given that ratio of conc. of Hln to ln^- ranges from 10 to $\frac{1}{10}$, then which of the following statements are correct ?
(A) Solution assumes P-colour, when $pH \le pK_{In} - 1$
(B) Solution assumes Q-colour, when $pH \ge pK_{In} + 1$
(C) Solution assumes P-colour, when $pH \ge pK_{In} - 1$
(D) Solution assumes Q-colour, when $pH \le pK_{In} + 1$

54. Which of the following statements is (are) correct ?

(A) A buffer solution contains a weak acid and its conjugate base

(B) A buffer solution show little changes in pH on the addition of a small amount of acid or base

(C) A buffer solution can be prepared by mixing a solution of sodium acetate and acetic acid

(D) The addition of solid potassium cyanide to water decrease the pH of water

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labeled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

55. **Match the Following:**

Column 1		Column 2	
(A)	$\underset{5\ ml\ 1N}{CH_3COOH} + \underset{5\ ml\ 1N}{NaOH}$	**(p)**	pH > 7
(B)	$\underset{15\ ml\ 1N}{CH_3COOH} + \underset{10\ ml\ 1N}{NaOH}$	**(q)**	pH < 7
(C)	$\underset{5\ ml\ 1N}{HCl} + \underset{15\ ml\ 1N}{NH_4OH}$	**(r)**	Buffer
(D)	$\underset{1\ ml\ 1N}{HCl} + \underset{1\ ml\ 2N}{NaOH}$	**(s)**	Hydrolysis occurs

56. **Match the Following:**

Column 1		Column 2	
(A)	50 ml of 0.1 M CH_3COOH + 25 ml of 0.1 M NaOH	**(p)**	Buffer solution
(B)	50 ml of 0.1 M NaOH + 50 ml of 0.1 M HCl	**(q)**	pH = 7 at 25°C
(C)	50 ml of 0.1 M NH_4OH + 25 ml of 0.1 M HCl	**(r)**	Basic solution
(D)	50 ml of 0.1 M CH_3COOH + 50 ml of 0.1 M NH_4OH ($K_a = K_b$)	**(s)**	Acidic solution

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

57. 500 ml of 0.150 M $AgNO_3$ solution is mixed with 500 ml of 1.09 M Fe^{2+} solution and the reaction is allowed to reach equilibrium at 25°C.

$$Ag^{+}(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

For 25 ml of the equilibrium solution, 30 ml of 0.0833 M $KMnO_4$ were required for oxidation. Calculate the approximate equilibrium constant for the reaction at 25°C.

58. An unknown volume and unknown concentration of weak acid HX is titrated with NaOH of unknown concentration. After addition of 10.0 cm^3 of NaOH solution, pH of solution is 5.7 and after the addition of 20.0 cm^3 of NaOH solution, the pH is 6.3. Calculate the pK_a for the weak acid, HX. (Given: antilog of 0.6 ≈ 4)

59. Waste water resulting from metal processing often contains significant amounts of toxic heavy metal ions that must be removed before the water can be safely returned to the environment. One method uses sodium hydroxide solution to precipitate insoluble metal hydroxides. Suppose that 1.00×10^2 L of waste water containing 1.8×10^{-5} M Cd^{2+} is treated with 1.0 L of 6.0 M NaOH solution. The residual concentration of Cd^{2+} after treatment is x $\times 10^{-12}$ M and the mass of $Cd(OH)_2$ precipitates is y gm. Identify x and y. (K_{sp} [$Cd(OH)_2$] = 2.5×10^{-14}) (atomic mass of Cd = 112)

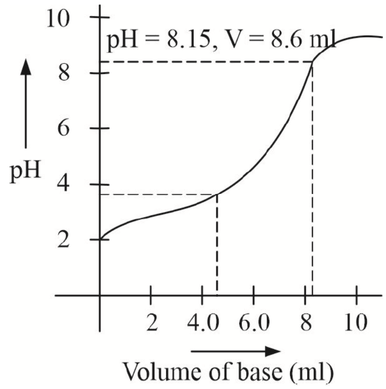
60. A mixture of water and AgCl is shaken until a saturated solution is obtained. Now the solution is filtered and 100 mL of clear solution of filtrate is mixed with 100 mL of 0.03 M NaBr. Ionic product of AgBr is x $\times 10^{-y}$ M. Find value of x. K_{sp} of AgCl and AgBr are 1×10^{-10} and 5×10^{-13}.

61. Given $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$. $K_c = 6.2 \times 10^{-8} M^2$ and K_{sp} of AgCl = 1.8×10^{-10} M^2 at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, the concentration of complex in 1.0 M aqueous ammonia is …….. M.

62. A solution is 0.1 M in Cl^-, 0.01 M in Br^-, 0.001 M in I^-. $AgNO_3(s)$ is added to the solution ($\Delta V_{mix} = 0$). The concentration of Ag^+ required to start precipitation of all three ions is 10^{-x} M. The numerical value of x is________.
[Given, $K_{SP(AgCl)} = 10^{-10}, K_{SP(AgBr)} = 10^{-13}, K_{SP(AgI)} = 10^{-17}$]

63. The pH of glycine at the first half equivalence point is 2.34 and that at second half equivalence paint is 9.60. At the equivalence point (the first inflection point) the pH is________.

64. Find the pK_a of a weak acid, if titration progress is monitored as follows:



65. The ionization constant of benzoic acid is 6.46×10^{-5} and K_{SP} for silver benzoate is 2.5×10^{-13}. How many times silver benzoate is more soluble in a buffer of pH = 3.19 as compared to its solubility in pure water?

Advanced Problem Package	Thermochemistry & Thermodynamics

SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. Based on the following thermochemical equations :

$H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$; $\Delta H = 131$ kJ

$CO(g) + 1/2\ O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -282$ kJ

$H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(g)$; $\Delta H = -242$ kJ

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = X$ kJ

The value of X will be :

(A) –393 kJ **(B)** – 655 kJ **(C)** + 393 kJ **(D)** + 655 kJ

2. From the reaction, $P_{(white)} \longrightarrow P_{(red)}$; $\Delta H = -18.4$ kJ it follows that :

(A) Red P is readily formed from white P
(B) White P is readily formed from red P
(C) White P cannot be converted to red P
(D) White P can be converted into red P and red P is more stable

3. Find $\Delta_f H°$ for HCl(g) from the following data:

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$; $\Delta_r H° = -176$ kJ/mole

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H° = -92$ kJ/mole

$N_2(g) + 4H_2(g) + Cl_2(g) \longrightarrow 2NH_4Cl(g)$; $\Delta_r H° = -629$ kJ/mole

(A) 536.5 kJ/mol **(B)** –361 kJ/mol **(C)** –92.5 kJ/mol **(D)** +92.5 kJ / mol

4. Solid $CaSO_4 \cdot 2H_2O$ is taken in a container fitted with a frictionless piston initially containing no other gases. The external pressure is maintained at 1 atm and the container is heated till the equilibrium is achieved.

$CaSO_4 \cdot 2H_2O(s) \rightleftharpoons 2CaSO_4(s) + 2H_2O\ (g)$

If $\Delta H° = +30$ Kcal/mol and $\Delta S° = +40$ cal / K, at what temperature equilibrium will be establised in the container. (Ignore variation of ΔH_0 and ΔS_0 with temperature.)

(A) 600 K **(B)** 750 K **(C)** 700 K **(D)** 300 K

5. Calculate the work done in Joules when 1.0 mole of N_2H_4 decomposes against a pressure of 1.0 atm at 27°C

$3N_2H_4(l) \longrightarrow 4NH_3(g) + 2N_2(g)$

(A) –4988.4 **(B)** –9976.8 **(C)** 9976.8 **(D)** None

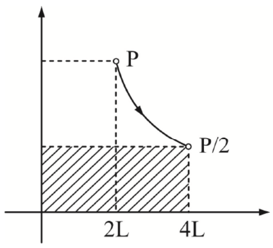
6. Calculate the heat produced (|q|) in kJ when 280 gm of CaO is completely converted to $CaCO_3$ by reaction with CO_2 at 27°C in a container of fixed volume. Given: ΔH_f^o $CaCO_3$ (s) = – 1207 kJ/mol ; ΔH_f^o CaO (s) = –635 kJ/mol ; ΔH_f^o CO_2 (g) = – 394 kJ/mol [Use R = 8.3 $JK^{-1}mol^{-1}$]

(A) 877.55 kJ **(B)** 87.755 kJ **(C)** 8775.5 kJ **(D)** None of these

7. 0.50 mol of an ideal gas initially at a temperature of 300 K and at a pressure of 2 atm is expanded isothermally in three steps. In each step, the pressure is dropped suddenly and held constant until equilibrium is reestablished. The pressure at each of the three stages of expansion are 1.6, 1.2 and 1 atm. Calculate the work done (|w|) (in atm-litre) in this process. [Use R = 0.08 atm-litre/mol.K]

(A) 7.4 atm litre **(B)** 4.7 atm litre **(C)** 6.2 atm litre **(D)** None of these

8. A student is calculating the work during a reversible isothermal process, shown by 2 moles of an ideal gas. He by mistake calculated the area as shown in the PV graph (Shaded area) equal to 49.26 litre atm. Calculate the correct value of work (in litre atm) during the process. (Given : R = 0.0821 litre atm/mol/K)



(A) 49.26 **(B)** – 34.14
(C) – 78.63 **(D)** – 98.52

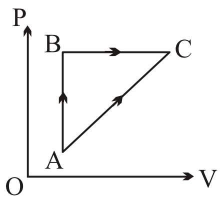
9. If the ratio $C_p/C_v = \gamma$, the change in internal energy of the mass of a ideal gas, when volume changes from V to 2V at constant pressure, P, is :

(A) $\frac{R}{\gamma-1}$ **(B)** PV **(C)** $\frac{PV}{\gamma-1}$ **(D)** $\frac{\gamma PV}{\gamma-1}$

10. Work done by a sample of an ideal gas in a process A is double of the work done in another process B. The temperature rises through the same amount in the two processes. If C_A and C_B be the molar heat capacities for the two processes

(A) $C_A = C_B$ **(B)** $C_A > C_B$ **(C)** $C_A < C_B$ **(D)** None of these

11. A thermodynamic process is shown in the following figure. In the process AB, 600J of heat is added to the system and in BC, 200J of heat is added to the system. The change in internal energy of the system in the process AC would be :
Given : $P_A = 3 \times 10^4$ Pa, $P_B = 8 \times 10^4$ Pa, $V_A = 2 \times 10^{-3}$ m^3, $V_C = 5 \times 10^{-3}$ m^3.



(A) 560 J **(B)** 800 J **(C)** 600J **(D)** 640 J

12. A reaction that is spontaneous can be described as:

(A) releasing heat to the surroundings
(B) having the same rate in both the forward and reverse directions
(C) proceeding in both the forward and reverse directions
(D) proceeding without external influence once it has begun

13. Calculate the standard enthalpy of formation of acetylene from the following data:

$C(g) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H° = -393.5$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H° = -285.8$ kJ mol^{-1}

$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$; $\Delta H° = -2598.8$ kJ mol^{-1}

(A) 226.6 kJ mol^{-1} **(B)** 230.5 kJ mol^{-1} **(C)** 233.8 kJ mol^{-1} **(D)** -226.6 kJ / mol

14. Which of the following statement(s) is(are) correct :
Statement **1** : The entropy of isolated system is always maximized at equilibrium
Statement **2** : It is possible for the entropy of close system to decrease in an irreversible process.
Statement **3** : Entropy can be created but can not be destroyed.
Statement **4** : ΔS_{system} is always zero for reversible process in an isolated system.

(A) Statement 1, 2, 3 **(B)** Statement 2, 4 **(C)** Statement 1, 2, 4 **(D)** All

15. The C – Cl bond energy can be calculated from :

(A) ΔH_f° (CCl_4, *l*) only

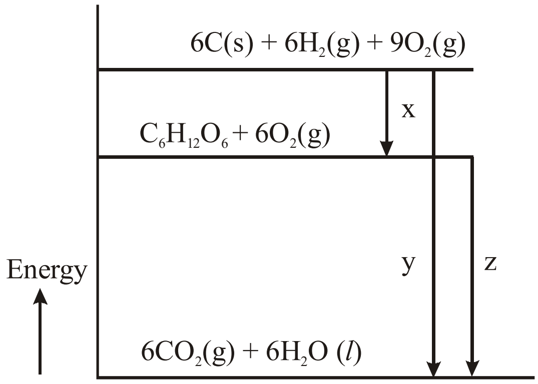
(B) ΔH_f° (CCl_4, *l*) and BE (Cl_2)

(C) ΔH_f° (CCl_4, *l*), BE (Cl_2)

(D) ΔH_f° (CCl_4, *l*) BE (Cl_2), ΔH_f° (C, g) and $\Delta H^\circ_{vap}(CCl_4)$

Paragraph for Questions 16 - 18

Paragraph # 1 : Consider the following energy level diagram :



Answer the following questions on the basis of the given diagram :

16. The heat of formation of glucose is :

(A) –x **(B)** –y **(C)** x – y **(D)** –x + z

17. In the given diagram z refers to :

(A) $6 \times \Delta H^o_{fCO_2}$

(B) $\Delta H^o_{fC_6H_{12}O_6}$

(C) $\Delta H^o_{combustion\ C_6H_{12}O_6}$

(D) $\Delta H^o_{combustion\ C(s)} + \Delta H^o_{fH_2O(l)}$

18. The quantity y is equal to :

(A) $\Delta H_{combustion\ C(s)} + \Delta H_{combustion\ H_2(g)}$

(B) x + z

(C) x – z

(D) $\Delta H_{fCO_2} + \Delta H_{H_2O}$

Paragraph for Questions 19 - 21

Heat capacity of a system is defined as the quantity of heat required to raise the temperature of the system by 1°C. If the mass of the system is one gm., the heat capacity is called the specific heat of the system. However, if the mass of the system is one mole, then the heat capacity is termed as molar heat capacity which is expressed by the differential equation $C = \frac{dQ}{dT}$

The molar heat capacity of a gaseous system, determined at constant volume (C_v) is different from that determined at constant pressure (C_P). In the former case, no external work is done by the system or on the system. Hence, from the first law equation

$$dQ = dE \qquad \therefore \qquad C_v = \left(\frac{dE}{dT}\right)_V$$

At constant pressure, there is change of volume and some work is done. Suppose, the volume increases by dV then

$$dQ = dE - dW = dE - (-PdV) = dE + PdV = dH \qquad \therefore \qquad C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$$

Let us consider a reaction occurring at constant pressure. Heat of reaction at constant pressure may be given as $\Delta H = H_P - H_R$

$$\frac{d\Delta H}{dT} = \frac{dH_P}{dT} - \frac{dH_R}{dT} = (C_P)_P - (C_P)_R = \Delta C_P$$

$d\Delta H = \Delta C_P \, dT$

Integrating above differential equation within proper limit we get : $\int_{T_1}^{T_2} d\Delta H = \Delta C_P \int_{T_1}^{T_2} dT$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$ This equation is called Kirchhoff's equation.

Read the paragraph carefully and answer the following questions:

19. The ratio of molar heat capacity of a monoatomic gas at constant pressure to that at constant volume is :

(A) 1.66 **(B)** 1.4 **(C)** 1.33 **(D)** 1.24

20. The molar heat capacity of argon at constant volume is 5 cal at 27°C. How much heat is required to raise the temperature of 20 gm of argon at constant pressure by 1°C?

(A) 1.5 cal **(B)** 2.5 cal **(C)** 3.0 cal **(D)** 5.0 cal

21. Which one of the following expressions is equal to heat capacity of a monoatomic gas at constant volume?

(A) $\left[\frac{\partial E}{\partial T}\right]_P$ **(B)** $\left[\frac{\partial T}{\partial P}\right]_H$ **(C)** $\left[\frac{\partial E}{\partial T}\right]_V$ **(D)** $\left[\frac{\partial E}{\partial H}\right]_T$

Paragraph for Questions 22 - 24

Entropy is the measure of degree of randomness. Entropy is directly proportional to temperature. Every system tries to acquire maximum state of randomness or disorder. Entropy is measure of unavailable energy.

Unavailable energy = Entropy × Temperature.

The ratio of entropy of vapourisation and boiling point of most liquids remains almost constant.

Read the paragraph carefully and answer the following questions:

22. Which of the following process have $\Delta S = -ve$?

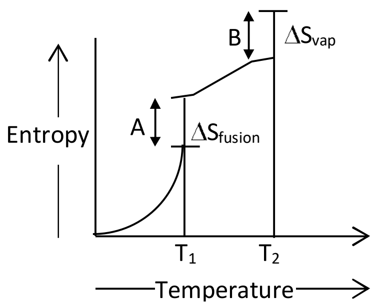
(A) Adsorption

(B) Dissolution of NH_4Cl in water

(C) $H_2 \rightarrow 2H$

(D) $2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

23. Observe the graph and identify the correct statement(s) :



(A) T_1 is melting point, T_2 is boiling point

(B) T_1 is boiling point, T_2 is melting point

(C) ΔS_{fusion} is more than ΔS_{vap}

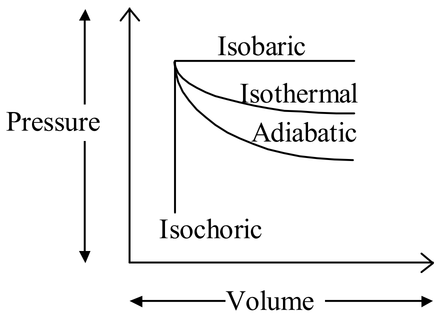
(D) T_2 is lower than T_1

24. The Law of thermodynamics invented by Nernst, which helps to determine absolute entropy, is :

(A) Zeroth law **(B)** 1st law **(C)** 2nd law **(D)** 3rd law

Paragraph for Questions 25 - 27

Observe the following graphic representation of four basic thermodynamic processes.



Read the paragraph carefully and answer the following questions:

25. Which of the following is true for isochoric process?

(A) $\Delta V = 0$ **(B)** $\Delta U = q + P\Delta V$ **(C)** $\Delta U = q_v$ **(D)** All of these

26. Which of the following is not true for isothermal process?

(A) $w_{exp} = -2.303nRT\log\frac{V_2}{V_1}$ **(B)** $w_{exp} = -2.303nRT\log\frac{P_1}{P_2}$

(C) $\Delta T = 0$ **(D)** $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

27. If the ratio $\frac{C_P}{C_v} = 1.30$ then the atomicity of gas will be:

(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

28. For an isolated system, the wall/boundary separating the system from surrounding must have the following characteristics:

(A) Rigid **(B)** Impermeable **(C)** Adiabatic **(D)** Diathermic

29. $\Delta E = 0$ for which process, must be zero

(A) Cyclic process **(B)** Isothermal ideal gas expansion

(C) Isochoric process **(D)** Adiabatic process

30. Select the correct option if temperature of a real gas is doubled at constant low pressure.

(A) Volume will be less than doubled if both temperature are above Boyle's temperature.

(B) Volume will be more than doubled if both temperature are less than Critical temperature.

(C) Volume will be less than doubled if both temperature are less than Critical temperature.

(D) None of these

31. Select the correct option(s) :

(A) Molar internal energy is an intensive property.

(B) Heat capacity at constant pressure is an extensive property

(C) Reversible process can be reversed at any point in the process by making infinitesimal change.

(D) Less heat is absorbed by the gas in the reversible isothermal expansion as compared to irreversible, when expanded to same final volume.

32. Pick out true statement among the following:
(A) Reversible adiabatic process is isoentropic process.
(B) ΔS_{system} for irreversible adiabatic compression is greater than zero.
(C) ΔS_{system} for free expansion is zero.
(D) ΔS_{surr} for irreversible isothermal compression is greater than zero.

33. Select the irreversible process(s)?
(A) Mixing of two gases by diffusion **(B)** Evaporation of water at 373 K and 0.1 atm pressure
(C) Free expansion of gases **(D)** None of these

34. Identify the incorrect statement regarding entropy :
(A) at absolute zero of temperature, the entropy of perfectly crystalline substance is +ve
(B) at absolute zero of temperature entropy of perfectly crystalline substance is taken to be zero
(C) at 0°C the entropy of a perfectly crystalline substance is taken to be zero
(D) at absolute zero of temperature, the entropy of all crystalline substances is taken to be zero

35. For which of the following substances, heat of formation in the standard state will not be zero?
(A) $Br_2(s)$ **(B)** $H^+(aq)$ **(C)** $Br_2(l)$ **(D)** $H_2O(l)$

36. For an isothermal irreversible expansion of 1 mole of a perfect gas, indicate the correct relation :
(A) $\Delta U = 0$ **(B)** $\Delta H = 0$ **(C)** $q = RT\left(1-\frac{P_2}{P_1}\right)$ **(D)** $w = RT\ln\left(\frac{P_2}{P_1}\right)$

37. $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -94.05 \text{ kcal mol}^{-1}$
$C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -94.5 \text{ kcal mol}^{-1}$
Then which of the following is / are correct ?
(A) $C_{(diamond)} \rightarrow C_{(graphite)}$; $\Delta H = 450 \text{ cal mol}^{-1}$ **(B)** $C_{(graphite)} \rightarrow C_{(diamond)}$; $\Delta H = 450 \text{ cal mol}^{-1}$
(C) graphite is more stable than diamond **(D)** diamond is more stable allotrope than graphite

38. Enthalpy of atomization of $C_2H_6(g)$ and $C_3H_8(g)$ are 620 and 880 kJ mol^{-1} respectively. The C–C and C–H bond energies are respectively.
(A) 80 and 60 kJ mol^{-1} **(B)** 80 and 90 kJ mol^{-1}
(C) 70 and 90 kJ mol^{-1} **(D)** 100 and 80 kJ mol^{-1}

39. In a process involving 'n' moles of an ideal gas, the entropy change of the system is given by :
(A) $nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ **(B)** $n\,C_P \ln\frac{T_2}{T_1} + n\,R\ln\frac{P_1}{P_2}$
(C) $n\,C_V \ln\frac{T_2}{T_1} + n\,R\ln\frac{P_1}{P_2}$ **(D)** $n\,C_V \ln\frac{T_2}{T_1} + n\,R\ln\frac{V_1}{V_2}$

40. Calculate the resonance energy for CO_2 from the following $\Delta H_{C=O} = 339 \text{ kJ mol}^{-1}$, $\Delta H_{O=O} = 498 \text{ kJ mol}^{-1}$, $\Delta H\left(C_{(s)} \longrightarrow C_{(g)}\right) = 718 \text{ kJ mol}^{-1}$, ΔH combustion (carbon) $= -393 \text{ kJ mol}^{-1}$
(A) 913 kJ mol^{-1} **(B)** – 931 kJ mol^{-1} **(C)** 145 kJ mol^{-1} **(D)** – 145 kJ mol^{-1}

41. Which of the following conclusion at equilibrium is(are) true?

(A) If $\Delta G° > 0$, $K_{eq} < 1$

(B) If $\Delta G°$ has a large negative value, the reaction will predominantly lie towards the product

(C) As the reaction proceeds towards equilibrium, Gibb's free energy change decreases and becomes zero finally

(D) As the reaction proceeds towards equilibrium, entropy of the system increases

42. Which of the following thermodynamic relations can be applied approximately to an ideal gas?

(A) $dE = dq + pdV$ **(B)** $dH = dq + Vdp$

(C) $dS_m = C_v \frac{dT}{T} + R\frac{dV}{V}$ **(D)** $dG = Vdp - SdT$

43. If an ideal gas in a piston fitted cylinder is allowed to expand isothermally against vacuum, then

(A) Expansion occur adiabatically **(B)** ΔS_{sys}, $\Delta S_{surr.}$, $\Delta S_{univ.}$ are all greater than zero

(C) $\Delta G < 0$ **(D)** $W_{sys.} = 0$

44. Which of the following statement(s) is(are) true?

(A) When $(\Delta G_{system})_{T, P} < 0$; the reaction must be exothermic

(B) $\Delta_f H°$ (S, monoclinic) $\neq 0$

(C) If dissociation energy of CH_4(g) is 1656 kJ/mole and C_2H_6 (g) is 2812 kJ/mole, then value of C–C bond energy will be 328 kJ/mole

(D) If $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; $\Delta_r H° = -56$ kJ/mol

$\Delta_f H°(H_2O, g) = -242$ kJ/mole; Enthalpy of vaporization of liquid water = 44 kJ/mol then, $\Delta_f H°(OH^-, aq)$ will be –142 kJ/mole

45. Which of the following conditions may lead to a non-spontaneous change ?

(A) $\Delta H = +ve$; $\Delta S = -ve$ **(B)** $\Delta H = -ve$; $\Delta S = -ve$

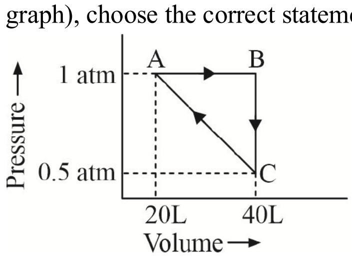
(C) $\Delta H = -ve$; $\Delta S = +ve$ **(D)** $\Delta H = +ve$; $\Delta S = +ve$

46. The work done during adiabatic expansion or compression of an ideal gas is given by :

(A) $nC_V \Delta T$ **(B)** $\frac{nR}{(\gamma - 1)}(T_2 - T_1)$

(C) $-nR\,P_{ext}\left[\frac{T_2P_1 - T_1P_2}{P_1P_2}\right]$ **(D)** $-2.303\,RT\log\frac{V_2}{V_1}$

47. On the basis of following graph (P–V graph), choose the correct statements.



(A) Total work done W = q

(B) The entropy change for the overall process is zero

(C) For the overall process $\Delta H > \Delta U$

(D) Total work done w > q

48. In which of the reaction $\Delta H > \Delta U$?

(A) $H_2 + I_2 \longrightarrow 2HI$ **(B)** $PCl_5 \longrightarrow PCl_3 + Cl_2$

(C) $2H_2O_2 \longrightarrow 2H_2O + O_2$ **(D)** $C + O_2 \longrightarrow CO_2$

49. Which of the following affect the heat of reaction ?

(A) Physical states of reactants and products
(B) Allotropic forms of elements
(C) Temperature
(D) Reaction carried out at constant pressure or constant temperature

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labeled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

50. Match the following:

	Column 1		Column 2
(A)	Isochoric process	**(p)**	$\Delta H = 0, \Delta E = 0, \Delta T = 0$
(B)	Isothermal reversible expansions	**(q)**	$w = 0,\ \Delta V = 0$
(C)	Adiabatic work done	**(r)**	$w = \frac{nR}{\gamma - 1}(T_2 - T_1)$
		(s)	$w = -nRT \ln V_2/V_1$

51. Match the solutions obtained by mixing different volumes of equimolar acid HA and base BOH given in column 1 with the rise in temperature given in column 2 if the solution obtained by mixing 10 ml each of the same acid and base shows an elevation in temperature of 5°C.

	Column 1		Column 2
(A)	100 ml of HA + 100 ml of BOH	**(p)**	5°C
(B)	10 ml of HA + 20 ml of BOH	**(q)**	4°C
(C)	20 ml of HA + 30 ml of BOH	**(r)**	3.3°C
(D)	50 ml of HA + 150 ml of BOH	**(s)**	0.66°C
		(t)	2.5°C

52. Match the following:

	Column 1		Column 2
(A)	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	**(p)**	heat of neutralization
(B)	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$	**(q)**	heat of combustion
(C)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	**(r)**	heat of formation
(D)	$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$	**(s)**	fuel cell

53. **Column-I** and **column-II** contains **four** entries each. Entries of column-I are to be matched with some entries of column-II. One or more than one entries of column-I may be matched with the same entries of column-II and one entry of column-I may have one or more than one matching with entries of column-II.

	Column 1		Column 2
(A)	For the process $H_2O(l) \rightleftharpoons H_2O(s)$, ΔH & ΔS are	**(p)**	–ve, +ve
(B)	For the endothermic reaction $2A(s) + ½\ O_2(g) \rightleftharpoons A_2O(s)$ at 298 K ΔS & ΔG are	**(q)**	+ve, –ve
(C)	C(diamond) $\rightleftharpoons$ C(graphite), favourable conditions for formation of diamond are high pressure and high temperature then ΔH for formation of diamond and ΔS for formation of graphite from diamond are	**(r)**	+ve, +ve
(D)	For the given reaction $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$, $E_{a(forward)}$= 57.2 kJ and $E_{a(backward)}$ = 3.2 kJ, ΔH for the given reaction & ΔS for the reverse reaction	**(s)**	–ve, –ve

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

54. If 2 kcal heat is given to a system and 6 kcal work is done on the system then the internal energy of system will increase by how many kcal?

55. Certain amount of a gas confined in a piston-filled cylinder is heated from 27°C to 127°C and the gas expanded against a constant pressure doing 4.157 kJ of work on surroundings. The number of moles of gas present in the cylinder is(are) __________.

56. Certain amount of a non-ideal gas is changed from state (500 K, 5 atm, 2 L) to (150 K, 2 atm, 1 L). If the change in internal energy is 14 L-atm, change in enthalpy in L-atm unit is __________.

57. Certain amount of an ideal gas confined in a 4.0 L piston at 20 K is allowed to expand adiabatically and reversibly to 25 L. If the ratio of heat capacities (molar heat capacity at constant pressure to molar heat capacity at constant volume) is 1.5, the final temperature (in Kelvin unit) of the gas would be __________.

58. Molar enthalpy of vaporization of a liquid is 3.6 kJ. If boiling point of this liquid is 177°C, the molar entropy of vaporization (in JK^{-1} unit) is __________.

59. When 1 mole of an ideal gas at 20 atm pressure and 15 L volume expands such that the final pressure becomes 10 atm and the final volume become 60 L. Calculate entropy change for the reaction $(C_{p.m} = 30.96)$ in $JK^{-1}mol^{-1}$.

(Given : $R = 8.314\,J\,mol^{-1}\,K^{-1}$)

60. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/°C. Then the enthalpy change in kJ during the process is : $(1L\ atm \simeq 100\ J)$

61. The given reaction

$$\underset{2\,\text{moles}}{2CO} + \underset{1\,\text{mole}}{O_2} \longrightarrow 2CO_2 \qquad \Delta H = -560\,\text{kJ}$$

is carried and in one litre container, if the pressure in the container gets changes from 70 atm to 40 atm as reaction gets completed. Calculate ΔU in kJ of the reaction. [1L atm = 0.1 kJ]

62. Calculate the pH at which the following conversion (reaction) will be at equilibrium in basic medium $I_2(s) \rightleftharpoons I^-(aq) + IO_3^-(aq)$ when the equilibrium concentrations at 300 K are $[I^-] = 0.10$ M and $[IO_3^-] = 0.10$ M

[Given that $\Delta G_f^0(I^-, aq) = -50$ kJ / mole, $\Delta G_f^0(IO_3^-, aq) = -123.5$ kJ / mole, $\Delta G_f^0(H_2O, \ell) = -233$ kJ / mole,

$\Delta G_f^0(OH^-, aq) = -150$ kJ / mole, Ideal gas constant $= R = \frac{25}{3}$ J mole^{-1}K^{-1}, $\log e = 2.3$]

Advanced Problem Package	Chemical Kinetics

SINGLE CORRECT ANSWER TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONLY ONE Choice is Correct.

1. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is :

(A) 4 **(B)** 3 **(C)** 2 **(D)** 1

2. For first order reaction: $A \longrightarrow P$, the temperature (T) dependent rate constant 'k' was found to follow the equation $\log_{10} k = 6 - \frac{2000}{T}$. The pre-exponential factor 'A' and activation energy E_a, respectively :

(A) $1\times10^6\ s^{-1}$ and 9.2 kJ mol^{-1} **(B)** $6.0 s^{-1}$ and 16.6 kJ mol^{-1}

(C) 1×0^6 and 16.6 kJ mol^{-1} **(D)** $1\times10^6 s^{-1}$ and 38.3 kJ mol^{-1}

3. The overall rate $\frac{d[P]}{dt}$, for the reaction $2A \underset{}{\overset{K}{\rightleftharpoons}} B;\ B + C \xrightarrow{k_f} P$ is given by :

(A) $K\ k_f\ [A]^2\ [C]$ **(B)** $K\ [A]\ [B]$ **(C)** $k_f\ [B]$ **(D)** $K\ k_f\ [A]^2\ [B]\ [C]$

4. For a first order reaction, if the time taken for 50% completion of the reaction is t seconds, then time required for 99.9% completion of the reaction is :

(A) 10 t **(B)** 5 t **(C)** 100 t **(D)** 2 t

5. The decomposition of a gas on a surface follows the rate law : Rate $\propto \frac{kP}{1+kP}$. Where, P is pressure and k is a constant. the order of the reaction at high pressure is :

(A) Zero **(B)** 1/2 **(C)** 1 **(D)** 2

6. For a gaseous reaction, the rate of reaction is expressed in terms of $\frac{dP}{dt}$ instead of $\frac{dC}{dt}$ or $\frac{dn}{dt}$, where C is concentration and n is the number of moles. Hence, the relation between expression is :

(A) $\frac{dC}{dt} = \frac{dn}{dt} = \frac{V}{RT}\frac{dP}{dt}$ **(B)** $\frac{dC}{dt} = \frac{1}{V}\frac{dn}{dt} = \frac{1}{RT}\frac{dP}{dt}$

(C) $\frac{dP}{dt} = \frac{dn}{dt} = \frac{dC}{dt}$ **(D)** None of these

7. For the reaction, $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

$$-\frac{d[NH_3]}{dt} = k_1[NH_3];\ \frac{d[N_2]}{dt} = k_2[NH_3];\ \frac{d[H_2]}{dt} = k_3[NH_3]$$

The relation between k_1, k_2 and k_3 may be given by as :

(A) $1.5\ k_1 = 3k_2 = k_3$ **(B)** $2k_1 = k_2 = 3k_3$ **(C)** $k_1 = k_2 = k_3$ **(D)** $k_1 = 3k_2 = 2k_3$

8. Rate constant for the reaction is $1.5\times10^7\ sec^{-1}$ at 50°C and $4.5\times10^7\ sec^{-1}$ at 100°C. What is the value of activation energy?

(A) 220 J mol^{-1} **(B)** 2300 J mol^{-1} **(C)** 2.2×10^3 J mol^{-1} **(D)** 2.2×10^4 J mol^{-1}

9. Which of the following is correct?
(A) Molecularity of a reaction can be fractional
(B) Zero order reaction never stops
(C) A first order reaction must be homogeneous
(D) The frequency factor 'A' in Arrhenius equation $\left(k = Ae^{-E_a/RT}\right)$ increases with increase in temperature

10. The order and molecularity of the chain reaction $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$, are :
(A) 2, 0 **(B)** 0, 2 **(C)** 1, 1 **(D)** 3, 0

11. A reactant, A forms two products:
$A \xrightarrow{k_1} B$ Activation energy E_{a_1} ; $A \xrightarrow{k_2} C$ Activation energy E_{a_2}
If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 will be related as :
(A) $k_2 = k_1 e^{-E_{a_1}/RT}$ **(B)** $k_2 = k_1 e^{-E_{a_2}/RT}$ **(C)** $k_1 = k_2 e^{-E_{a_1}/RT}$ **(D)** $k_1 = 2k_2 e^{-E_{a_2}/RT}$

12. Collision theory is satisfactory for :
(A) First order reactions **(B)** Second order reactions
(C) Bimolecular reactions **(D)** Zeroth order reactions

13. Consider the following statements :
1. The rate of reaction is always proportional to the concentrations of reactants.
2. The order of an elementary chemical reaction step can be determined by examining its stoichiometry.
3. The first order reactions follows an exponential time course.
Of these statements :
(A) 1, 2 and 3 are correct **(B)** 1 and 2 are correct
(C) 2 and 3 are correct **(D)** 1 and 3 are correct

14. For a gaseous reaction, the following data were recorded :

Concentration in $mol\ L^{-1}$	0.1	0.05	0.025	0.0125
Half-life in sec	30	29.9	30.1	30

The order of reaction is :
(A) Second **(B)** First **(C)** Zero **(D)** Fractional

15. Consider the reaction : $2NO_2(g) + O_3(g) \longrightarrow N_2O_5(g) + O_2(g)$
The reaction of nitrogen dioxide and ozone represented is first order in $NO_2(g)$ and in $O_3(g)$. Which of these possible reaction mechanisms is consistent with the rate law?

Mechanism I: $NO_2(g) + O_3 \longrightarrow NO_3(g) + O_2(g)$ (slow)
$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$ (fast)

Mechanism II: $O_3(g) \rightleftharpoons O_2(g) + [O]$ (fast)
$NO_2(g) + [O] \longrightarrow NO_3$ (slow)
$NO_3(g) + NO_2(g) \longrightarrow N_2O_5$ (fast)

(A) I only **(B)** II only **(C)** Both I and II **(D)** Neither I nor II

16. In which of the following reactions, the increase in the rate of reaction will be maximum?

	E_a	Temperature rise
(A)	40 kJ/mol	$200-210$ K
(B)	90 kJ/mol	$300-320$K
(C)	80 kJ/mol	$300-310$ K
(D)	All will have same rate	

17. For nth order reaction $\frac{t_{1/2}}{t_{3/4}}$ depends on $(n \neq 1)$:

(A) Initial concentration only **(B)** 'n' only
(C) Initial concentration and 'n' both **(D)** Sometimes 'n' and sometimes initial concentration

18. Half-life of a reaction becomes half when *initial*concentration of reactants are made double. The order of reaction will be :

(A) 1 **(B)** 2 **(C)** 0 **(D)** 3

19. Decomposition of H_2O_2 is a first order reaction. A 16 volume solution of H_2O_2 of half life 30 min is present at start. When will the solution become one volume?

(A) After 120 min **(B)** After 90 min **(C)** After 60 min **(D)** After 150 min

20. What is the activation energy for the reverse of this reaction?

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$

Data for the given reaction is $\Delta H = +54$ kJ and $E_a = +57.2$ kJ :

(A) −54 kJ **(B)** +3.2 kJ **(C)** +60.2 kJ **(D)** +111.2 kJ

21. Consider the reaction, $2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$

The rate law for this reaction is:Rate = k $[H_2]$ $[NO]^2$

Under what conditions could these steps represent the mechanism?

Step 1 : $2NO \rightleftharpoons N_2O_2$ **Step 2 :** $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$

Step 3 : $N_2O + H_2 \longrightarrow N_2 + H_2O$

(A) These steps cannot be the mechanism under any circumstances
(B) These steps could be the mechanism if step 1 is the slow step
(C) These steps could be the mechanism if step 2 is the slow step
(D) These steps could be the mechanism if step 3 is the slow step

22. The acid catalysed ionisation of $\gamma-$hydroxy butyric acid proceeds as a reversible reaction,which is 1st order in both the forward and backward steps : $\underset{(Acid)}{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(Lactose)}{B}$

The rate $-\frac{d[A]}{dt}$ is given by :

(A) $k_1[A]$ **(B)** $-k_2[B]$ **(C)** $k_1[A]-k_2[B]$ **(D)** $\frac{k_1[A]}{k_2[B]}$

23. What is the slope of the straight line for the graph drawn between ln k and 1/T, where k is the rate constant of the reaction at temperature T?

(A) $\frac{-E_a}{2.303\,R}$ **(B)** $\frac{-E_a}{R}$ **(C)** $\frac{E_a}{R}$ **(D)** $\frac{R}{E_a}$

24. The correct statement regarding the functioning of a catalyst is that it:

I $\rightarrow$ alters the energy levels of the reactants and products.

II $\rightarrow$ provides an alternate path for climbing the activation energy barrier.

III $\rightarrow$ makes the reaction thermodynamically feasible.

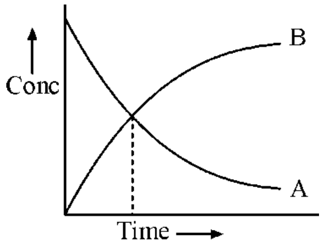
IV $\rightarrow$ provides a different mechanism of the reaction.

(A) I and II **(B)** I and III

(C) II and IV **(D)** III and IV

25. The following plot represents the variation of the concentration of a species A and B against time

Reaction : $A \longrightarrow B$.



The point of intersection of the two curves represents :

(A) $t_{1/2}$ **(B)** $t_{3/4}$

(C) $t_{2/3}$ **(D)** $t_{1/3}$

26. The specific rate constant of a first order reaction depends on the :

(A) Concentration of the reactant **(B)** Concentration of the product

(C) Time **(D)** Temperature

Reasoning Type - For Questions 27-29

(A) Statement-1 is True, Statement-2 is True and Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True and 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.

27. **Statement : 1** In a multi-step reaction, the molecularity of overall reaction has no significance.

Statement : 2 Molecularity refers to the order of rate determining step.

28. **Statement : 1** Order of a reaction may be fractional.

Statement : 2 Sum of power of concentration terms involved in rate law expression gives the order of reaction.

29. **Statement : 1** Hydrolysis of ethyl acetate in acid medium is pseudo first order reaction.

Statement : 2 $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$. Water does not take part in this reaction.

Paragraph for Questions 30 - 32

The reaction rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of reactant per unit time. However, also because of stoichiometry of the balanced chemical reaction, rate of reactions in terms of individual reactants and products are related.

30. Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

The rate of reaction may be expressed as :

(A) rate $= -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = +\frac{d[NH_3]}{dt}$ **(B)** rate $= -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$

(C) rate $= -\frac{d[N_2]}{dt} = +\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$ **(D)** rate $= -\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = +2\frac{d[NH_3]}{dt}$

31. For a chemical reaction, $m_1A + m_2B \longrightarrow n_1C + n_2D$. The ratio of rate of disappearance of A to that of appearance of C is :

(A) m_1/m_2 **(B)** m_2/n_1 **(C)** n_1/m_1 **(D)** m_1/n_1

32. In the following reaction : $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

The rate of formation of SO_3 is 100 g min^{-1}. Hence, the rate of disappearance of $O_2$is :

(A) 50 g min^{-1} **(B)** 20g min^{-1} **(C)** 100 g min^{-1} **(D)** 200 g min^{-1}

Paragraph for Questions 33 - 36

The reactions occurring in two or more steps are called complex reactions. Each step however is a simple reaction, i.e., an elementary reaction.The rates of the various elementary reactions generally differ from one another. The rate of the reaction is determined from slowest step. The chemical species present in rate law expression, must also be present in overall reaction.

33. The reaction, $2O_3(g) \longrightarrow 3O_2(g)$, proceeds as follows :

$O_3(g) \rightleftharpoons O_2 + [O]$ (fast) ; $[O] + O_3 \longrightarrow 2O_2$ (slow)

The rate law expression should be :

(A) $r = k[O_3]^2$ **(B)** $r = k[O_3]^2[O_2]^{-1}$ **(C)** $r = k[O_2]^2$ **(D)** $r = k[O_3][O_2]$

34. The reaction, $2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$, follows the mechanism given ahead :

Step 1 : $NO + Br_2 \rightleftharpoons NOBr_2$ (fast) **Step 2 :** $NOBr_2 + NO \longrightarrow 2NOBr$ (slow)

The overall order of this reaction is :

(A) 2 **(B)** 1 **(C)** 3 **(D)** None of these

35. A reaction, $A_2 + B_2 \longrightarrow 2AB$, occurs in following steps :

Step 1 : $A_2 \longrightarrow A + A$ (slow) **Step 2 :** $A + B_2 \longrightarrow AB + B$ (fast)

Step 3 : $A + B \longrightarrow AB$ (fast)

The order of reaction would be :

(A) 3/2 **(B)** zero **(C)** 2 **(D)** 1

36. In the following consecutive reactions, $A \xrightarrow{k = 2\times10^{-4}\ min^{-1}} B \xrightarrow{k = 6\times10^{-6}\ min^{-1}} C \xrightarrow{k = 3\times10^{-3}\ min^{-1}} D$

Which of the following steps is the rate determining step ?

(A) $A \rightarrow B$ **(B)** $B \rightarrow C$ **(C)** $C \rightarrow D$ **(D)** $A \rightarrow D$

MULTIPLE CORRECT ANSWERS TYPE

Each of the following Question has 4 choices A, B, C & D, out of which ONE or MORE Choices may be Correct:

37. For a first order reaction :

(A) The degree of dissociation is equal to $\left(1-e^{-kt}\right)$

(B) A plot of reciprocal concentration of the reactant vs time gives a straight line

(C) The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction

(D) The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

38. The rate law for the reaction, $RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by Rate = k_1[RCl]. The rate of the reaction will be:

(A) Doubled on doubling the concentration of sodium hydroxide

(B) Halved on reducing the concentration of alkyl halide to one half

(C) Increased on increasing the temperature of the reaction

(D) Unaffected by increasing the temperature of the reaction

39. For the first order reaction : $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

(A) The concentration of the reactant decreases exponentially with time.

(B) The half-life of the reaction decreases with increasing temperature.

(C) The half-life of the reaction depends on the initial concentration of the reactant.

(D) The reaction proceeds to 99.6% completion in eight half-life duration.

40. Which of the following statements are correct about the reaction in presence of catalyst?

(A) Catalyst does not alter the heat of reaction

(B) Catalyst alters the equilibrium constant of the reaction

(C) Catalyst does not alter the $\Delta G°$ of the reaction

(D) Catalyst changes the rate constant of forward and backward reaction to the same extent.

41. In the Arrhenius equation, $k = Ae^{-E_a/RT}$, the Arrhenius constant A will be equal to the rate constant when

(A) $E_a = 0$ **(B)** $T = \infty$ **(C)** $T = 0$ **(D)** $E_a = \infty$

42. Rate law expression of a reaction is :Rate = k $[A]^{2/3}[B]$

Which of the following are correct about the corresponding reaction?

(A) Order of reaction = $\frac{2}{3} + 1 = \frac{5}{3}$ **(B)** Unit of rate constant = $L^{2/3}\,mol^{-2/3}\,sec^{-1}$

(C) Unit of rate constant = $L^{-2/3}\,mol^{2/3}\,sec^{-1}$ **(D)** Unit of rate of reaction = $mol\,L^{-1}\,sec^{-1}$

43. Which of the following are correct expression for Arrhenius equation?

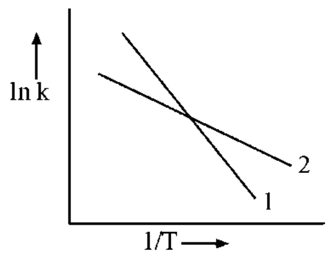
(A) $A = ke^{-E_a/RT}$ **(B)** $\ln k = \ln A + \frac{E_a}{RT}$

(C) $\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$ **(D)** $\ln A = \ln k + \frac{E_a}{RT}$

44. A substance 'A' may react to give different products in two different path :

(1) $A \xrightarrow{k_1} B + C$ (2) $A \xrightarrow{k_2} D + E$

Both these reactions paths are of first order and have identical frequency factor. If k is plotted against 1/T for (1) and (2) :



Select the correct statements among following :

(A) Activation energy of reaction (1) is greater than that of (2)
(B) Activation energy of reaction (2) is greater than that of (1)
(C) B and C are favourable product
(D) D and E are favourable products

45. Which of the following are true for the first order reaction?

(A) $t_{3/4} = 2t_{1/2}$ **(B)** $t_{15/16} = 4t_{1/2}$ **(C)** $t_{15/16} = 3t_{3/4}$ **(D)** $t_{7/8} = 2t_{3/4}$

46. Activation energy of forward and backward process of a reaction are 60 kJ and 40 kJ mol^{-1} respectively. Which of the following are true for the reaction?

(A) It is endothermic reaction **(B)** It is exothermic reaction
(C) Heat of reaction is +20 $kJ\,mol^{-1}$ **(D)** Threshold energy of reaction is 100 $kJ\,mol^{-1}$

47. Select the correct statement(s) among following :

(A) Increase in concentration of reactant increases the rate of a zero order reaction
(B) Rate constant k is equal to collision frequency A, if $E_a = 0$
(C) Rate constant k is equal to collision frequency A if $E_a = \infty$
(D) $\log_{10} k$ vs $1/T$ is a straight line

MATRIX MATCH TYPE

Each of the following question contains statements given in two columns, which have to be matched. Statements in Column 1 are labelled as (A), (B), (C) & (D) whereas statements in Column 2 are labeled as p, q, r, s & t. More than one choice from Column 2 can be matched with Column 1.

48. **Match the following:**

Column 1 (Half – life)		**Column 2 (Order of reaction)**	
(A)	$t_{1/2}$ = constant	**(p)**	First order
(B)	$t_{1/2} \propto a$	**(q)**	Pseudo first order
(C)	$t_{1/2} \propto \frac{1}{a}$	**(r)**	Second order
(D)	$t_{1/2} \propto \frac{1}{p}$	**(s)**	Zero order

a = Initial concentration of reactant ; p = Initial pressure of gaseous reactant

Numerical Value Type Questions

The Answer to the following questions can be positive or negative integers of 1/2/3 digits, 0 and decimal numerical value.

49. For the reaction, $A_2 + B_2 \longrightarrow 2AB$

$[A_2]$	$[B_2]$	Rate of reaction (mol L^{-1} sec^{-1})
0.2 M	0.2 M	0.04
0.1 M	0.4 M	0.04
0.2 M	0.4 M	0.08

Order of reaction will be ______ .

50. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10} = 2.3$)

51. In a reaction, the time required to complete half of the reaction was found to increase 16 times when the initial concentration of the reactant was reduced to 1/4th. What is the order of the reaction?

52. If the $t_{1/2}$ for a first order reaction is 0.4 min, the time after 99.9% completion of the reaction is _______ min.

53. A reaction $X_2(g) \longrightarrow Z(g) + \frac{1}{2}Y(g)$ exhibits an increase in pressure from 150 mm to 170 mm in 10 min. The rate of disappearance of X_2 in mm per min is ______.

54. Rate constant of reaction increases (2^n) times. Temperature coefficient of this reaction is '2'. Initial and final temperature of the reaction is 25°C and 115°C respectively. What will be the value of 'n' ?

55. The rate of reaction, $3A + 2B \longrightarrow$ Products is given by rate expression, rate $= k[A][B]^2$. If 'A' is taken in excess, the order of the reaction would be_______.

56. In a catalytic conversion of N_2 to NH_3 by Haber's process, the rate of reaction expressed as change in the concentration of ammonia per unit time is 40×10^{-3} mol L^{-1} s^{-1}. If there are no side reaction, the rate of the reaction as expressed in terms of hydrogen is $y \times 10^{-3}$ mol L^{-1} s^{-1}. Find value of y.

57. In the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, initial pressure is 500 atm and rate constant k is 3.38×10^{-5} sec^{-1}. After 10 minutes the final pressure (in atm) of N_2O_5 is________.

58. The rate constant for an isomerization reaction, $A \rightarrow B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1M. The rate of the reaction after 1h is $y \times 10^{-3}$ M min^{-1}. Find value of y.

59. A first order gas reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change into the product?

60. The rate constant for a second order reaction is 8.0×10^{-5} M^{-1} min^{-1}. How many minutes will it take a 1M solution to be reduced to 0.5 M ?

61. 0.1 g atom of radioactive isotope ${}_{Z}X^{A}$ (half-life 5 days) is taken. The number of atoms that will decay during eleventh day are $y \times 10^{21}$ atoms. Find value of y.

61. A certain nuclide has a half-life period of 30 minutes. If a sample containing 600 atoms is allowed to decay for 90 minutes, how many atoms will remain.

62. Radioactive decay follows first order kinetics. After 90 min, i.e. after three half lives

$600 \xrightarrow{30\,\text{min}} 300 \xrightarrow{30\,\text{min}} 150 \xrightarrow{30\,\text{min}} 75$

$\therefore$ 75 atoms will be left

63. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5×10^9 years). The age of the rock would be $y \times 10^9$ years. Find value of y.

64. For reaction $A \rightarrow B$, $\Delta H = -10\,\text{kJ mol}^{-1}$, $E_a = 50\,\text{kJ mol}^{-1}$, then E_a in kJ/mol of $B \rightarrow A$ will be________.

65. Radioactivity of a radioactive element remains $\frac{1}{10}$ of the original radioactivity after 2.303 seconds. The half life period in second is :

66. In the Lindemann theory of unimolecular reactions, it is shown that the apparent rate constant for such a reaction is $k_{app} = \frac{k_1 C}{1 + \alpha C}$ here C is the concentration of the reactant, k_1 and α are constants. The value of C for which k_{app} has 90% of its limiting value at C tending to infinitely large values, given $\alpha = 9 \times 10^5$ is 10^{-x} mol L^{-1}. Find value of x.

67. With the help of following information

Rate (forward) = $(1.45 \times 10^{13})[Fe^{2+}][diPy]^3$

Rate (backward) = $(1.22 \times 10^{-4})\left[Fe(dipy)_3^{2+}\right]$

and $Fe^{2+} + 3\,dipy \rightarrow Fe(dipy)_3^{2+}$ the stability constant for the complex will be $y \times 10^{17}\ M^{-2}$. Find value of y.

68. Biochemists often define Q_{10} for a reaction as the ratio of the rate constant at 37°C to the rate constant at 27°C. What must be the energy of activation in kJ mol^{-1} for a reaction that has $Q_{10} = 2.5$?

69. A drop of solution (Volume 0.05 ml) contains 3.0×10^{-6} mole of H^+. If the rate constant of disappearance of H^+ is 1.0×10^{7} mol lt^{-1} sec^{-1}. It takes $y \times 10^{-9}$ sec for H^+ drop to disappear. Find value of y.

70. The following kinetic data are provided for a reaction between A and B :

Concentration of A/(M)	**Concentration of B/(M)**	**Rate of reaction (M min^{-1})**
0.50	0.02	1.15×10^{-4}
0.50	0.04	2.30×10^{-4}
0.01	1.00	2.30×10^{-6}
0.02	1.00	0.92×10^{-5}

Then value of the rate constant for the above reaction is equal to $y \times 10^{-2}\ L^2\ mol^{-2}\ min^{-1}$. Find value of y.

71. 99% of first order reaction was completed in 32 min. Find time in min for 99.9% completion of reaction.

72. The rate of the reaction : $A + B + C \longrightarrow$ Product is given by :

$\text{rate} = -\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/4}[C]^0$

The order of reaction is________.

73. The reaction $A \longrightarrow B$ follows first order reaction. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time in hour taken for conversion of 0.9 mole of A to produce 0.675 moles of B :

74. The rate constant for the forward and backward reactions of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute respectively. The equilibrium constant of the reaction is ________.

75. For a reaction the activation energy $Ea = 0$ and the rate constant $k = 3.2 \times 10^6 s^{-1}$ at 300 K. The value of rate constant at 310 K is found to be $y \times 10^6 s^{-1}$. What is value of y?

76. The conversion of $A \to B$ follows second order reaction. Doubling the concentration of A will increase the rate of reaction by ________ times.