

SECTION III: COMPREHENSIONS

COMPREHENSION # 1

Paragraph for Questions Nos. 56 to 58

In the quantum mechanics there is operator (\hat{A}) for every physically observable property like momentum (linear or angular), position, K.E., total energy etc., and whenever the function (ψ) is operated upon by the operator of any property, we get back ψ multiplied by a constant (a) which is the value of the property under consideration. The function ψ obeying the condition is called eigenfunction of the operator \hat{A} and the constant " a " is called eigen-value. Mathematically

$$\hat{A}\psi = a \cdot \psi$$

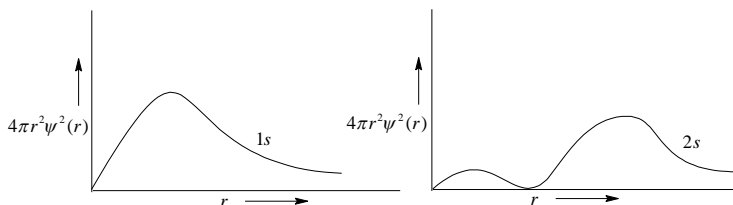
This equation is called eigen-value equation.

The Schrodinger wave equation is the energy eigen value equation. The operator for total energy is called Hamiltonian operator (H) defined as

$$H = -\frac{h^2}{8\pi^2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V$$

Where V = PE, m = mass of microparticle.

Solving Schrodinger wave equation for H-atom after putting proper value of V , we get wave functions (ψ) and corresponding energy values. Each wave function denotes an orbital. ψ^2 measures the probability of finding the electron and $\psi^2 dx$ gives the probability of finding the electron in the region x and $x + dx$. $4\pi r^2 \psi^2(r) dr$ gives the probability of finding the electron in spherical shell of thickness dr at a distance r from the nucleus. A plot of radial distribution function $[4\pi r^2 \psi^2(r)]$ vs. distance from the nucleus (r) gives the radial probability distribution curve of electron. For 1s and 2s orbitals each containing only one electron, these curves are as given below



The wave functions of 1s and 2s orbitals of hydrogenic atom or ion are given below:

$$\psi_{1s} = 2 \left(\frac{Z}{a_0} \right)^{1/2} e^{-Zr/a_0}$$

$$\psi_{2s} = \left(\frac{Z}{2a_0} \right)^{1/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

In 2s-orbital there occurs a point at the radius at which curve touches X-axis. Here the probability of finding the electron is zero. This is called radial node.

On the basis of the above write-up, answer the following questions:

56. Which of the functions given below is not the eigen function of the operator $\frac{d^2}{dx^2}$?
 (A) e^{-3x} (B) $\sin 4x$ (C) $4x^2$ (D) $\cos 2x$
57. An electron moves along x-axis and restricted to move only between $x = 0$ and $x = L$. Hence
 (A) $\int_0^L \psi^2 dx = 1$ (B) $\int_0^L \psi^2 dx = 0$ (C) $\int_0^L \psi^2 dx > 1$ (D) $\int_0^L \psi^2 dx < 1$
58. An electron is moving along X-axis in absence of any external field. The energy eigen-value of electron with $\psi = e^{-5x}$, is
 (a) $\frac{25}{8} \frac{h^2}{\pi^2 m}$ (b) $\frac{3}{8} \frac{h^2}{\pi^2 m}$ (c) $\frac{h^2}{8\pi^2 m}$ (d) $\frac{h^2}{4\pi^2 m}$

COMPREHENSION # 2

Paragraph for Questions Nos. 59 to 60

From the Bohr's model and De-broglie's theory it can be proved that number of waves in an orbit is equal to its principal quantum nos.(n). The orbital motion of the electron around the nucleus is described by angular momentum of the electron which is characterised by azimuthal quantum number, l. l have all possible whole number values from 0 to $n - 1$ and magnitude of angular

momentum is given by $(\ell / \ell + 1)^{1/2} \hbar$. The various sub shells are distributed as s, p, d, f, ...

according to the value of $l = 0, 1, 2, 3, \dots$ respectively.

Angular momentum about the z-axis is quantised and given by z-component of angular momentum $= m_\ell \hbar$ where $m_\ell = \ell(\ell + 1)^{1/2} \cos \theta$ and is known as magnetic quantum number. Possible values of m range from $-l$ through 0 to $+l$, thus making a total of $2l + 1$ values. The possible values of m indicates the number of degenerate orbitals in a given energy sub level within a principal energy level.

59. When the value of $l = 1$, then the values of θ are
 (A) $60^\circ, 120^\circ, 180^\circ$ (B) $0, 90^\circ, 180^\circ$ (C) $45^\circ, 90^\circ, 135^\circ$ (D) $30^\circ, 60^\circ, 90^\circ$
60. The difference between orbital angular momentum of a 2s and a 3d electron is
 (A) $\sqrt{2}\hbar$ (B) 0 (C) $\sqrt{4}\hbar$ (D) $\sqrt{6}\hbar$

COMPREHENSION # 3

Paragraph for Questions Nos. 61 to 63

The radial probability at a distance r from the nucleus is given by the function $4\pi r^2 \psi^2 dr$. In this function, as the probability factor ψ^2 decreases, the volume factor $4\pi r^2 dr$ increases with increase in value of r . The probability increases gradually as the distance increases, goes to a maximum and then begins to decrease. For $1s$ orbital of hydrogen atom, the maximum value is found by differentiating radial probability distribution with respect to r and setting the derivative equal to zero as

$$\frac{dP(r)}{dr} = \frac{4}{a_0^3} \left[-\frac{2r^2}{a_0} + 2r \right] e^{-2e/a_0} = 0.$$

The radial motion of an electron in an atom is controlled by the centrifugal force $\ell(\ell + 1)/r^3$ as well as by coulombing force of attraction $(-Ze^2/r^2)$ or

$$\frac{\ell(\ell + 1)}{r^3} - \frac{Ze}{r^2} = 0$$

61. The probability of radial distribution function of an electron is zero becomes possible when distance r is equal to
- (A) 0.529\AA (B) zero (C) $2 \times 0.529\text{\AA}$ (D) $\frac{0.529}{2}\text{\AA}$
62. In two different cases under similar conditions, an electron tends to stay farther from the nucleus in case I with respect to case II. It shows that
- (A) Orbital angular momentum in, case I $>$ case II
(B) Orbital angular momentum in, case I $<$ case II
(C) Orbital angular momentum in, case I $=$ case II
(D) None of the above
63. The electron distribution in $1s$ orbital is found to be symmetrical. Considering θ and ϕ be the angles involved in polar coordinate, it may be concluded that:
- (A) ψ_{1s}^2 is dependent on θ (B) is dependent on ϕ
(C) is dependent on both θ and ϕ (D) is independent of θ and ϕ

COMPREHENSION # 4

Paragraph for Questions Nos. 64 to 67

In CBSE XII, a question was asked which reads as follows:

Dry air contains 80% N_2 and 20% O_2 by volume. Calculate density of dry air at 27°C and 1 atm pressure.

If relative humidity of moist air is 50% and V.P. of water at 27°C is 40 mm. Calculate the density (g/L) of moist air also. Assume ideal behavior of each gas. Relative humidity is defined as the ratio of the partial pressure of moisture in air to its V.P.

Three students "X", "Y" and "Z" solved 1st part of the problem in the following three different ways:

Solution of "X": One litre dry air contains 0.8 L N_2 and 0.2 L O_2 at the partial pressure of 0.8 atm and 0.2 atm respectively while each at 27°C i.e. 300K. He then calculated number of mole (n) of each gas using the ideal gas equation $PV = nRT$. He then multiplied number of mole with respective MW to get the mass of each gas in gram. Adding the masses of the two gases he was able to find the mass of 1 litre air in gram and the same he reported as the density of dry air.

Solution of "Y": One litre dry air contains 0.8 L N_2 and 0.2 L O_2 each at a pressure of 1.0 atm and temperature of 27°C i.e. 300K. Thereafter he followed the same method as adopted by "X" and reported the density of dry air.

Solution of “Z”: One litre dry air may be supposed to contain 1.0 L each of N_2 and O_2 at $27^\circ C$ but at a partial pressure of 0.8 atm and 0.2 atm, respectively. Then he followed the method as adopted by his aforesaid guys, and reported the density of dry air.

64. The correct solution(s) is (are) that of:
 (A) both X and Y (B) both Y and Z (C) All the three (D) Only X
65. If solution “X” is wrong what conceptual mistake he has committed:
 (A) Boyle’s law is violated (B) Charle’s law is violated
 (C) Graham’s law is violated (D) There is no violation of any gas law
66. If solution “Y” is wrong what conceptual mistake he has committed:
 (A) Dalton’s law of partial pressure is violated
 (B) Avogadro’s hypothesis has been violated
 (C) Boyle’s law is violated
 (D) There is no violation of any gas law
67. Solution of “Z” is wrong because
 (A) Boyle’s law is violated (B) Charle’s law is violated
 (C) Avogadro’s hypothesis is violated (D) The solution is correct

COMPREHENSION # 5

Paragraph for Questions Nos. 68 to 70

Compressibility factor (Z): Real gases deviate from ideal behaviour due to the following two faulty assumptions of kinetic theory of gases.

- Actual volume occupied by the gas molecule is negligible as compared to the total volume of the gases.
 - Forces of attraction and repulsion among the gas molecules are negligible.
- To explain, the extent of deviation of the real gas from ideal behaviour in terms of compressibility or, compression factor (Z), which is function of pressure and temperature for real gases.

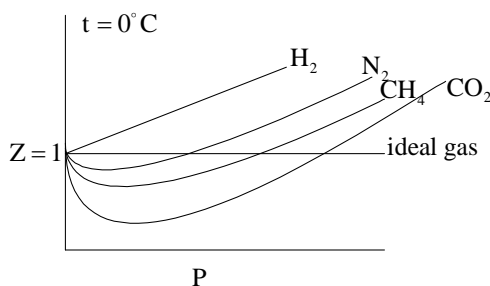
$$Z = \frac{P_0 V_0}{nRT}$$

For ideal gases $Z = 1$

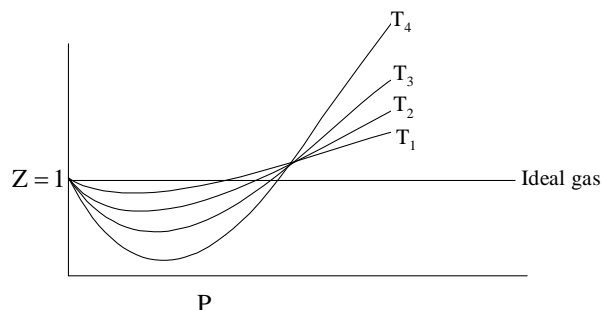
For real gases either $Z > 1$ or $Z < 1$

When $Z > 1$, then it is less compressible because force of repulsion dominates over force of attraction when $Z < 1$, force of attraction dominates over the force repulsion and it is more compressible.

Graph in between Z & P is shown as under



On increasing temperature, Z increases and approaches to unity. Graph between Z and P at different temperature for the same gases are as under:



68. Which of the following statements are correct?
- (A) The compressibility factor for ideal gases dependent on temperature and pressure.
- (B) $\left(\frac{dZ}{dP}\right)_T$ for real gas is independent of pressure.
- (C) for all real gases have same value
- (D) for different real gases have different values.
69. Which of the following is the correct order of temperature shown in the above graph Z vs P for the same gases.
- (A) $T_4 > T_3 > T_2 > T_1$
- (B) $T_1 > T_2 > T_3 > T_4$
- (C) $T_1 > T_2 > T_4 > T_3$
- (D) $T_3 > T_4 > T_2 > T_1$
70. Which of the following statements is correct for gas A having molar mass 16 g and density 0.75 g/litre at 2 atmospheric pressure and 27°C temperature?
- (A) Force of attraction are dominating than force of repulsion among the gas molecules.
- (B) Force of repulsion are dominating than force of attraction among the gas molecules.
- (C) Gas molecules are behaving ideally
- (D) None

COMPREHENSION # 6

Paragraph for Questions Nos. 71 to 73

The van der waal's equaiton of state for 1 mole real gas is ... (i)

The virial equation for 1 mole real gas is as under:

Where A, B and C are constants which are known as 2nd, third and fourth virial coefficients respectively.

Since we known that $V=f(P, T, n)$

Since ideal gas equation for 1 mole ideal gas is

$$PV = RT \quad \dots(ii)$$

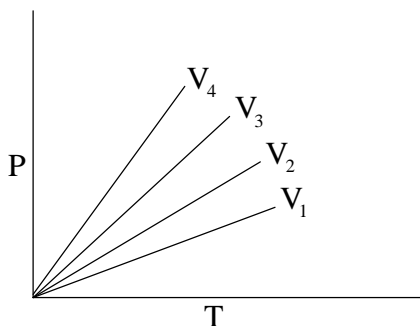
The temperature at which real gas obey ideal gas equation is known as Boyle's temperature i.e. T_B .

71. If equation (ii) be one of the form of equation (i), then value of "A" will be
- (A) $b - \frac{a}{RT}$
- (B) $a - \frac{b}{RT}$
- (C) $RT - \frac{a}{b}$
- (D) $\frac{RT \times b}{a}$
72. Which of the following is the correct statement about the Boyle's temperature (T_B)?
- (A) Temperature at which second virial coefficient becomes zero
- (B) Temperature at which first virial coefficient becomes zero
- (C) The value of T_B is equal to $\frac{a}{Rb}$
- (D) Both (a) and (c) are correct

73. The ideal gas equation for 1 mole of ideal gas is given as under

$$PV = nRT$$

The graph is drawn in between P and T for different isochoric process, or different constant volume, which gives different straight lines shown as under:



then which of the following is the correct order of volume?

- (A) $V_4 > V_3 > V_2 > V_1$ (B) $V_1 > V_2 > V_3 > V_4$
 (C) $V_1 > V_2 > V_4 > V_3$ (D) $V_2 > V_1 > V_3 > V_4$

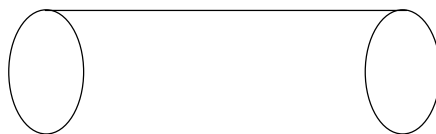
COMPREHENSION # 7

Paragraph for Questions Nos. 74 to 76

Diffusion is the one of the most striking property of the gas, due to which one gas intermixes with other against gravity at low pressure gradient at constant temperature. And according to Graham, rate of diffusion of a diffusing gas is inversely proportional to the square root of the density or molecular mass of the diffusing gas i.e.,

$$r \propto \frac{1}{\sqrt{d}} \propto \frac{1}{\sqrt{m}} \quad \dots(i)$$

The rate of diffusion inside an open tube is directly proportional to the length



$$r = \frac{v}{t} = \left(\frac{A}{t} \right) \times \text{length}$$

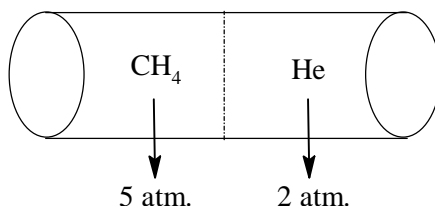
$$r \propto \text{length}$$

But, effusion is a special kind of diffusion, possible at high pressure gradient only. It is a kind of forced diffusion. Infact, incase of effusion rate of intermixing will be influenced by pressure gradient. So, in effusion pressure must be considered i.e.,

$$r \propto \frac{P}{\sqrt{m}} \propto \frac{P}{\sqrt{d}}$$

74. At the start of an experiment one end of a U-tube of 6 mm glass tubing is immersed in conc. NH_3 solution and the other end is immersed in conc. HCl solution. At the point in the tube where vapours of NH_3 and HCl meet, a white cloud of NH_4Cl (s) forms. At what fraction of the distance along the tube from the NH_3 solution does the white cloud first form?
- (A) 0.068 (B) 6.82 (C) 0.422 (D) 4.22

75. A long cylindrical glass tube, equipped with a process disc at the centre contain CH_4 gas at 5 atm. on one side and He gas at 2 atm on the other side of the disc as shown in the diagram.



Disc is permeable to both gases and rate of diffusion is directly proportional to the gas pressure and inversely proportional to square root of molar masses as;

$$-\frac{dP}{dt} = \frac{kP}{\sqrt{M}}$$

If K for the CH_4 is $2.5 \times 10^{-2} \text{ sec}^{-1}$, determine time after which pressure of CH_4 chamber will drop to 4 atm?

- (A) 8.778 sec. (B) 87.88 sec. (C) 48.2 sec. (D) 40 sec.
76. If a space capsule is filled with Ne gas at 1 atm and 290K. The gas effuses through a pin-hole into outer space at such a rate that the pressure drops by 0.30 torr/s. If the capsule were filled with NH_3 at the same temperature and pressure what would be the rate of pressure drop?
- (A) 0.33 torr/s (B) 0.20 torr/s (C) 0.13 torr/s (D) 3.3 torr/s

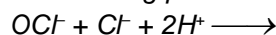
COMPREHENSION # 8

Paragraph for Questions Nos. 77 to 79

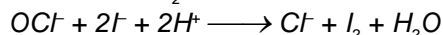
“Percentage of available chlorine in the sample of blaching power”

Bleaching powder is a mixture of calcium hypochlorite (CaOCl_2) and the basic chloride $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ free slaked lime is also present in addition.

Available chlorine in bleaching powder is the amount of chlorine liberated by the action of dilute acids on bleaching powder according to the equation.



The available chlorine is expressed as the percentage by weight of the bleaching powder. It is measured by iodometric titration. The bleaching powder solution or suspension is treated with an excess of KI and then acidified with acetic acid where I_2 is liberated



The liberated I_2 is determined with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as indicator near the end point



77. 0.05 moles of CaOCl_2 reacts with excess of KI and liberated I_2 is titrated with V ml of 0.1M hypo solution then value of V is
- (A) 500 ml (B) 1000 ml (C) 2000 ml (D) 250 ml
78. A 20 ml (specific gravity 1.02) of chlorine water is treated with excess of KI and the liberated Iodine required 25 ml of 0.2 N $\text{Na}_2\text{S}_2\text{O}_3$. The percentage of free chlorine in chlorine water is
- (A) 0.87 (B) 87 (C) 0.78 (D) 0.82
79. The volume of 0.2 M $\text{Na}_2\text{S}_2\text{O}_3$ equivalent to I_2 liberated by the oxidation of excess KI by 10 millimole of bleaching powder (pure) is
- (A) 50 ml (B) 20 ml (C) 25 ml (D) 100 ml

COMPREHENSION # 9

Paragraph for Questions Nos. 80 to 83

Like acid base titration, in redox titration also, the equivalence point is reached when the reducing agent is completely oxidized by the oxidizing agent. But contrary to the acid-base titrations, oxidizing agents can themselves be used as internal indicator in redox titration e.g. $\text{Cr}_2\text{O}_7^{2-}$ (orange yellow), Cr^{3+} (green), MnO_4^- (purple), Mn^{2+} (light pink), where strength of the solution may be expressed as molarity i.e. number of moles of solute per litre of solution.

80. In a titration experiment, a student finds that 23.48 ml of a NaOH solution are needed to neutralize 0.5468g of KHP (molecular formula $\text{KHC}_8\text{H}_4\text{O}_4$). What is the concentration in molarity of NaOH solution?
(A) 0.114 M (B) 0.228M (C) 0.057M (D) 0.028 M
81. A 16.42 ml volume of 0.1327M KMnO_4 solution is needed to oxidize 25.00 ml of a FeSO_4 solution in an acidic medium. What is the number of moles of FeSO_4 being oxidized for the reaction
$$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$$

(A) 2.18×10^{-2} ml (B) 1.09×10^{-2} ml (C) 0.545×10^{-2} ml (D) 0.272×10^{-2} ml
82. A purple coloured solution is added from a burette to FeSO_4 solution kept in the flask. After sometime, the purple colour changes to light pink. The ion formed from that solution is
(A) MnO_4^- (B) Fe^{2+} (C) Fe^{3+} (D) Mn^{2+}
83. Concentrated aqueous sulphuric acid is 98% H_2SO_4 by mass and has a density of 1.84 g/ml. What volume of the concentrated acid is required to make 5 litre of 0.50M H_2S_4 solution.
(A) 271.7 ml (B) 13.5 ml (C) 135.85 ml (D) 27.1 ml

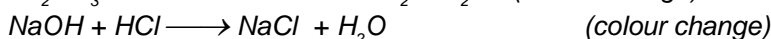
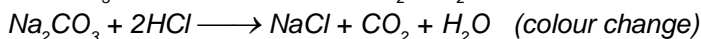
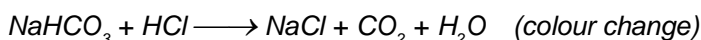
COMPREHENSION # 10

Paragraph for Questions Nos. 84 to 86

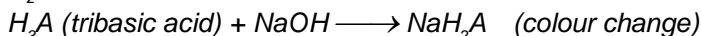
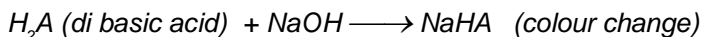
Double Titration

1. Methyl orange as an indicator

The volume of 0.1 NHCl used in the titration will correspond the neutralization as directed.



The volume of 0.1M NaOH in the titration will neutralize as directed

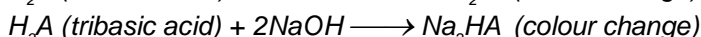
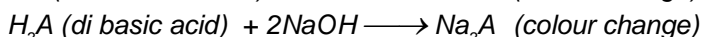


2. Phenolphthelien as an indicator

The volume of 0.1 NHCl used in the titration will correspond the neutralization as directed.



The volume of 0.1M NaOH in the titration will neutralize as directed



84. 0.01 mole of H_3PO_4 and 0.01 mole H_3PO_2 reacts with V ml standard NaOH in presence of phenolphthelien indicator volume of NaOH used is
 (A) 500 ml (B) 400 ml (C) 300 ml (D) 200 ml
85. 20 ml of x M HCl neutralizes completely 10 ml of 0.1 M solution and a further 5 ml of 0.2 M solution to methyl orange end point. The value of x is:
 (A) 0.167 M (B) 0.133 M (C) 0.15 M (D) 0.2 M
86. Certain moles of is dissolved in excess of NaOH. The resulting solution is divided into two equal parts. One part needs 30 ml of 2.5 N HCl and other part needs 40 ml of 2.5 N HCl using phenolphthalein and methyl orange indicator respectively. The mass of dissolved is:
 (A) 2.5×10^{-2} (B) 5×10^{-2} (C) 10×10^{-2} (D) 1.5×10^{-2}

COMPREHENSION # 11

Paragraph for Questions Nos. 87 to 89

Bond length is the average distance between the nuclei of the two atoms held by a bond. This represents the internuclear distance corresponding to minimum potential energy for the system. Main factors which affect the bond length are given below:—

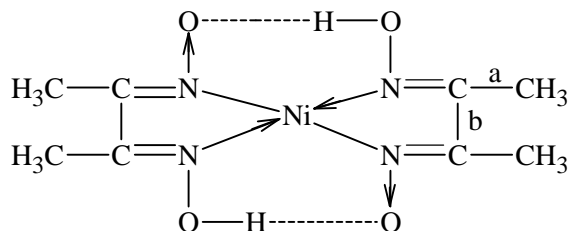
- Multiple bonds are shorter than corresponding single bonds
- Sometimes single bond distances are some what larger than double of their respective covalent radii (e.g. F_2). It is due to strong repulsive interaction between the lone-pair electrons on adjacent atoms.
- Some times single bond distances are some what shorter than double of their respective covalent radii because bonds acquire some partial double bond character. This normally happens when one atom having vacant orbital and another atom containing lone pair. It is also possible it become shorter due to high ionic character in the covalent bond.

87. Which is not true about the N – N bond length among the following species
 I. $\text{H}_2\text{N} - \text{NH}_2$ II. N_2
 III. $\text{H}\overset{+}{\text{N}} - \text{NH}_2$ IV. N_2O
 (A) N – N bond length is shortest in II
 (B) N – N bond length in I is shorter than that of in III
 (C) N – N bond length in III is shorter than that of in I
 (D) N – N bond length IV is intermediate between I and III
88. The correct order about of C—O bond length is
 I. CO , II. CO_2 III. CO_3^{2-}
 (A) $\text{II} < \text{I} < \text{III}$ (B) $\text{III} < \text{II} < \text{I}$ (C) $\text{I} < \text{II} < \text{III}$ (D) $\text{I} < \text{III} < \text{II}$
89. The bond angle is Cl_2O is more than that in F_2O because of so many reasons like
 (a) $p_\pi - d_\pi$ overlap in Cl_2O which is not possible in F_2O
 (b) There is no lp – lp repulsion in Cl_2O which is present in F_2O
 (c) F is more electronegative than oxygen while Cl is less electronegative than oxygen
 The correct reason is (are)
 (A) both a and b (B) only a (C) only b (D) all the three

COMPREHENSION # 12

Paragraph for Questions Nos. 90 to 92

"Dimethyl glyoxime is an important reagent, which is used in the detection of Ni^{2+} ion in fourth group of qualitative analysis and also in its gravimetric estimation. The compound formed by Ni^{2+} ions with dimethyl glyoxime is diamagnetic with the structure as given below.



'a' and 'b' are C—C bond length".

90. Which of the following is correct regarding the bond length 'a' and 'b'.
- (A) $a = b$ (B) $a > b$ (C) $b > a$ (D) none of the above
91. The necessary conditions for the formation of intramolecular hydrogen bonding is
- (A) The ring formed as a result of hydrogen bond should be planar
 (B) A five or six membered ring should be formed
 (C) Interacting atoms should be placed in such a way that there is minimum strain during the ring formation
 (D) All of these
92. The atomic orbitals which the central atom is using in hybridisation are:
- (A) $4s, 4p_x, 4p_y$ and $4p_z$ (b) $3d_{z^2}, 4s, p_x$ and $4p_y$
 (C) $3d_{x^2-y^2}, 4s, 4p_x$ and $4p_y$ (d) $3d_{x^2-y^2}, 4s, 4p_y$ and $4p_z$

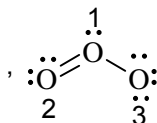
COMPREHENSION # 13

Paragraph for Questions Nos. 93 to 95

The formal charge is the difference between the number of valence electrons in an isolated (i.e. free) atom and the number of electrons assigned to that atom in a Lewis structure. While as a result of polarization, the molecule possesses a dipole moment which is the product of charge on the dipole and distance between them. For a molecule, the net dipole moment is the vector addition of all the dipole moment. Just as all the covalent bonds have some partial ionic character the ionic bonds also have partial covalent character. The polarizing power of the cation, the polarisability of the anion and the extent of distortion of anion are the factors, which determine the percent covalent character of the ionic bond.

93. Experiment shows that H_2O has a dipole moment whereas CO_2 has not. Point out the structures which best illustrate these factor.
- (A) $\text{O} = \text{C} = \text{O}$, $\text{H} - \text{O} - \text{H}$ (B) $\text{O} = \text{C} = \text{O}$, $\text{H} - \text{O} - \text{H}$
 (C) $\text{O} = \text{C} = \text{O}$, $\text{H} - \text{O} - \text{H}$ (D) $\text{O} = \text{C} = \text{O}$, $\text{H} - \text{C} - \text{H}$

94. It has been seen that in O_3 , the central O atom is bonded to two other oxygen atoms as



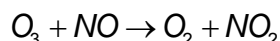
Arrange oxygen atoms marked as 1, 2 and 3 in order of their decreasing formal charge:

- (A) $1 < 2 < 3$ (B) $1 > 3 > 2$ (C) $1 > 2 > 3$ (D) $2 > 1 > 3$
95. Among $LiCl$, $BeCl_2$, BCl_3 and CCl_4 , covalent bond character follows the order:
- (A) $LiCl > BeCl_2 > BCl_3 > CCl_4$ (B) $LiCl < BeCl_2 < BCl_3 < CCl_4$
 (C) $LiCl > BeCl_2 > CCl_4 > BCl_3$ (D) $LiCl < BeCl_2 < BCl_3 > CCl_4$

COMPREHENSION # 14

Paragraph for Questions Nos. 96 to 98

The depletion of ozone in the stratosphere has been a matter of great concern among scientists in recent years. It is believed that ozone can react with nitric oxide (NO) that is discharged from the high altitude jet plane. The reaction is:



96. If 0.740 g of O_3 reacts with 0.670 g of NO, how many gram of NO_2 will be produced ?
 (A) 0.71 g (B) 0.74 g (C) 0.68 g (D) 0.81 g
97. Which compound is the limiting reactant?
 (A) NO (B) O_3
 (C) Both are in equimolar ratio (D) Both are in stoichiometric ratio
98. Number of moles of the excess reactant remaining at the end of the reaction is
 (A) 0.007 mol O_3 (B) 0.014 mol O_3 (C) 0.007 mol NO (D) 0.014 mol NO

COMPREHENSION # 15

Paragraph for Questions Nos. 99 to 101

8.7 gm of a sample of is used in a chemical reaction with HCl to release . Released is used to displace from excess of KI solution. The iodine hence released is estimated using hypo and consumes 100 ml of hypo solution.. 12.5 ml of same hypo solution is required for complete reaction with 25 ml of 0.5 N solution.

99. % purity of is
 (A) 4.35 (B) 43.5 (C) 50 (D) 6.25
100. Wt. of which may be completely neutralized by the amount of HCl made to react quantitatively with pure in the sample is
 (A) 106 g (B) 10.6 g (C) 5.3 g (D) 53 g
101. Number of milli moles of iodine in the solution used with hypo are
 (A) 6.25 (B) 12.5 (C) 10 (D) 20

COMPREHENSION # 16

Paragraph for Questions Nos. 102 to 104

Whenever any solute is dissolved in a given solvent, a solution is formed. Solution may be homogeneous or heterogeneous. Homogeneous solution is termed as true solution and in this concentration of solution is defined as mole or mass of solute present in the given weight or volume of solution. Units which depend on mass are temperature independent while which depend on volume are temperature dependent. Answer following question after reading passage—

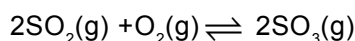
102. Which of the following unit is temperature dependent
(A) molality (B) ppm (C) mole fraction (D) molarity
103. If aqueous solution of KOH contains 28% by weight of KOH hence mole fraction of KOH is
(A) (B) (C) (D)
104. Mass of glucose ($C_6H_{12}O_6$) present in 50 ml of its 2 molar solution is
(A) 18000 gm (B) 180 gm (C) 18 gm (D) 1800 gm

COMPREHENSION # 17

Paragraph for Questions Nos. 105 to 108

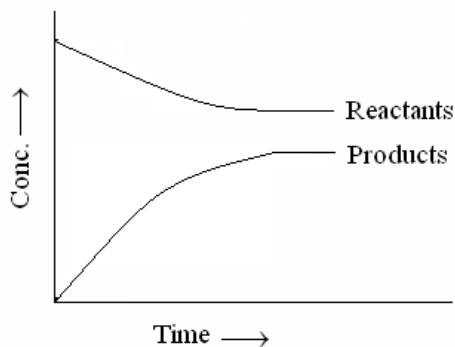
In a reversible chemical reaction, the rate of forward reaction decreases and that of backward reaction increases with the passage of time; at equilibrium the rate of forward and backward reactions become same.

Let us consider the formation of SO_3 in the following reversible reaction:

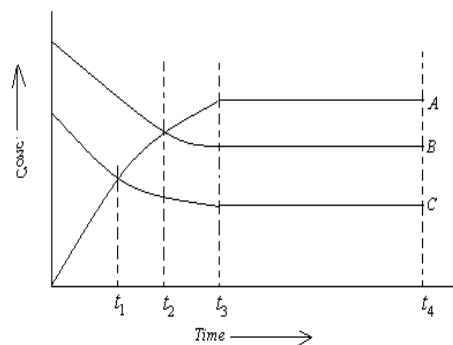


Following graphs are plotted for this reaction:

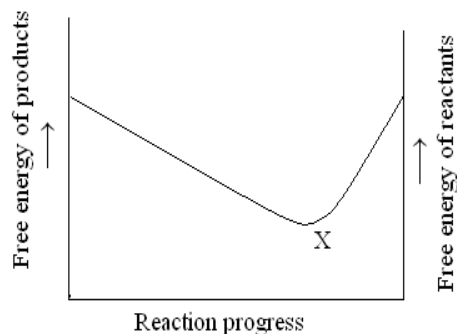
Graph - 1



Graph - 2



Graph - 3



105. In the graph(1), the equilibrium state is reached at:
 (A) t_1 (B) t_2 (C) t_3 (D) t_4
106. If pressure decreases when the reaction is in the state of equilibrium, then the reaction may shifted towards–
 (A) SO_3
 (B) SO_2 & O_2
 (C) No change as all the molecules are gases
 (D) Not specified
107. The graph(2) tells us that:
 (A) equilibrium is never achievable
 (B) equilibrium is achieved after the concentrations of reactants and products become equal
 (C) equilibrium is achieved before the concentrations of reactants and products become equal
 (D) none of these
108. From the graph(3), it can be interpreted that:
 (A) equilibrium is achieved at X (B) reaction is nearer to the completion
 (C) $\Delta G=0$ at X (D) all of the above

COMPREHENSION # 18

Paragraph for Questions Nos. 109 to 111

When 306 g of NH_4HS is introduced in a 4.1 litre evacuated flask and heated to $227^\circ C$ then solid NH_4HS decomposes into gaseous ammonia and hydrogen sulphide. At equilibrium, it is found that 170 gm of H_2S are present in the container.

109. Mass of solid remaining in the container is -
 (A) 51 g (B) 136 g (C) 68 g (D) 100 g
110. If after establishment of equilibrium, H_2S is added in the container in such a way that partial pressure of H_2S now equals to original total pressure, then partial pressure of NH_3 at new equilibrium is -
 (A) 50 atm (B) 25 atm (C) 100 atm (D) 75 atm
111. If at $227^\circ C$, ammonia also starts decomposing into nitrogen and hydrogen and establishes equilibrium ($2NH_3 \rightleftharpoons N_2 + 3H_2$) then K_p for the reaction $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ and total pressure developed in the container will -
 (A) decreases, increases (B) increases, decreases
 (C) no change, no change (D) no change, increases

COMPREHENSION # 19

Paragraph for Questions Nos. 112 to 114

Law of mass action can also be applied to the study of equilibria in which the substances are not in the same phase. Considering the decomposition of solid $NaHCO_3$ to produce solid Na_2CO_3 , gaseous CO_2 and H_2O .



Applying the law of mass action.

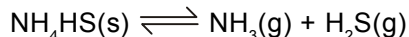
$$K_c' = \frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]^2}$$

It involves two pure solids, Na_2CO_3 and NaHCO_3 . It is customary not to include the concentrations of pure solids in equilibrium expressions.

$$\frac{K'_c[\text{NaHCO}_3]^2}{[\text{Na}_2\text{CO}_3]} = [\text{CO}_2][\text{H}_2\text{O}] \quad \text{or} \quad K_c = [\text{CO}_2][\text{H}_2\text{O}]$$

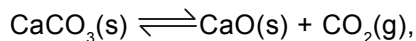
In terms of partial pressures we have $K_p = P_{\text{CO}_2} \times P_{\text{H}_2\text{O}}$. Similarly, in reactions in which a reactant or product occurs as a pure liquid phase, the concentration of that substance in the pure liquid is also constant. As a result, the concentrations of pure solid and pure liquid phases do not appear in the equilibrium constant expression.

112. Ammonium hydrogen sulphide dissociates according to the equation



If the observed pressure at equilibrium is 2280 torr atm at 380 K, what is the equilibrium constant K_p of the reaction?

- (A) 1.5 (B) 2.25 (C) 3 (D) 4.5
113. A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K_p if total pressure at equilibrium is 0.8 atm.
- (A) 1.8 atm (B) 0.8 atm (C) 3.6 atm (D) 4 atm
114. A sample of $\text{CaCO}_3\text{(s)}$ is introduced into a sealed container of volume 0.64 litre and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction,



is 4×10^{-2} atm at this temperature. Calculate the mass of CaO (in mg) present at equilibrium.

- (A) 3.584 (B) 1.792 (C) 17.92 (D) 35.84

COMPREHENSION # 20

Paragraph for Questions Nos. 115 to 117

Buffer Solutions : In general, a buffer solution is one which is resistant to change of pH upon the addition of a small amount of acid or alkali. Such solutions usually consist of a mixture of a weak acid and salt of its conjugate base, e.g. HAc and NaAc (called acidic buffers), or of a weak base and salt of its conjugate acid, e.g. NH_4OH and NH_4Cl (called basic buffers). A salt of a weak acid and a weak base, e.g. NH_4Ac , also has a buffer action.

The pH of an acidic buffer and basic buffer is expressed by Henderson-Hasselbalch equations

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \quad \text{pOH} = \text{pK}_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

But limitations of the above equations is that it works only for buffer solutions that fit the following criteria

- * The ratio, $[\text{conjugate base}] / [\text{weak acid}]$ has a value between 0.1 and 10.
- * Both $[\text{conjugate base}]$ and $[\text{weak acid}]$ exceed K_a by a factor of 100 or more.

The resistance to the change in pH, on the addition of an acid or alkali is called 'Buffer action'. This

buffer action is measured by 'Buffer capacity' (β). It is expressed as $\beta = \frac{db}{dpH}$

where db is no. of moles of base added to one litre buffer solution and dpH is change in pH. The buffer capacity (β) is maximum when the acid and the salt are present in equal concentrations.

115. The acetate-acetic acid buffer is suitable in the pH range (assume K_b of $\text{CH}_3\text{COO}^- = 10^{-9}$)
- (A) 8 – 10 (B) 4 – 6 (C) 5 – 7 (D) 5.5 – 7.5

116. A solution of pH = 6 will be maintained by acidic buffer. Below are the few options given to a chemist. Which option will the chemist choose ?
 (A) HA (0.1 M), NaA (1M) K_b of $A^- = 10^{-9}$ (B) HB (0.01 M), NaB (1 M) K_b of $B^- = 10^{-10}$
 (C) HC (1 M), NaX (0.01 M) K_b of $X^- = 10^{-6}$ (D) Any one of the above
117. pH of a mixture of 1 M benzoic acid ($pK_a = 4.20$) and 1 M C_6H_5COONa is 4.5 what is the volume of benzoic acid required to prepare a 300 ml buffer [$\log 2 = 0.3$] ?
 (A) 200 ml (B) 150 ml (C) 100 ml (D) 50 ml

COMPREHENSION # 21

Paragraph for Questions Nos. 118 to 117

In a mixture of strong acid and a strong base, concentration of H^+ ions or OH^- ions can be calculated as

$[H^+] \text{ or } [OH^-] = \text{meq of S.A} - \text{meq of S.B} / \text{total volume in ml of the mixture or volume given}$
 At equivalence point of titration of a strong acid with strong base pH=7 at 25°C. Salt formed does not undergo salt hydrolysis.

In case of weak acid with strong base, before the equivalence point, pH is calculated using the concept of acid buffer. At the equivalence point pH is calculated taking into consideration salt hydrolysis. $pH = \frac{1}{2}(pK_w + pK_a + \log C)$

Beyond the equivalence point, there is excess of base, which mainly determines the pH. In case of weak base with strong acid, before the equivalence point buffer concept is used, at the equivalence point salt hydrolysis is taken into consideration.

$pH = \frac{1}{2}(pK_w - pK_b - \log C)$

In case of titration of weak acid and weak base at equivalence point pH is calculated on the basis of salt hydrolysis $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$

118. 100ml of 0.1 M mono acid weak base, $K_b = 2 \times 10^{-5}$ is titrated with 0.1M HCl. pH of the reaction mixture at the titre value of 50ml and 100 ml are respectively.
 (A) 9.3, 9.3 (B) 9.3, 6.6 (C) 9.3, 5.3 (D) 4.7, 6.6
119. When 50ml of 0.2M HA, $K_a = 1.0 \times 10^{-5}$ is mixed with 50ml of 0.2M KOH at 25°C pH of the resulting mixture would be
 (A) 9.0 (B) 9.15 (C) 8.50 (D) 8.2
120. 100ml of 0.1M HCl is titrated with 0.1M NaOH. The pH of the reaction mixture after the addition of 50ml, 100ml, 150ml are respectively
 (A) 1.3, 7.0, 9.23 (B) 1.48, 7.0, 12.3 (C) 1.7, 7.0, 12.3 (D) 7.0, 1.3, 12.3

COMPREHENSION # 22

Paragraph for Questions Nos. 121 to 123

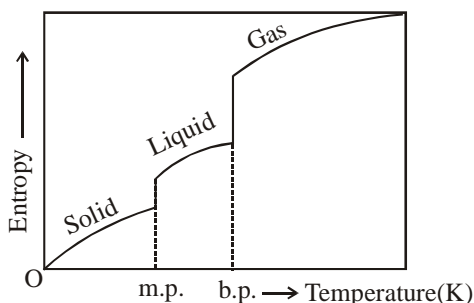
K_{sp} of $CdS = 8 \times 10^{-27}$, K_{sp} of $ZnS = 1 \times 10^{-21}$, K_a of $H_2S = 1 \times 10^{-21}$

121. Which metal sulphide is precipitated first when H_2S is added
 (A) ZnS (B) CdS
 (C) Both at same time (D) Both do not form ppt.
122. What $[H^+]$ must be maintained in a saturated $H_2S(0.1M)$ to precipitate CdS but not ZnS , if $[Cd^{+2}] = [Zn^{+2}] = 0.1M$ initially
 (A) $> 0.1M$ (B) $> 0.01M$ (C) $> 0.2M$ (D) $> 0.02M$
123. When ZnS starts precipitating. What is the concentration of Cd^{+2} is left
 (A) 8×10^{-7} (B) 0.1 (C) 4×10^{-10} (D) 2×10^{-9}

COMPREHENSION # 23

Paragraph for Questions Nos. 124 to 126

Entropy is associated with the orientation and distribution of molecules in space. Disordered crystals have higher entropy than ordered crystals and diffused gases have higher entropy than compressed gases.



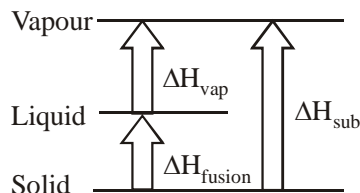
Entropy is also associated with molecular motion. As the temperature of a substance increases, random molecular motion increases hence entropy increases. Figure gives variation of entropy with temperature. At absolute zero (-273°C) every substance is in solid state whose particles are rigidly fixed in a crystalline structure. If there is no residual orientational disorder, like that in CO, entropy of the substance at 0 K will be zero. Third law of thermodynamics states that. **“At the absolute zero of temperature the entropy of every substance may become zero and does become zero in case of perfectly crystalline structure.”**

$$\lim_{T \rightarrow 0} s = 0$$

In case of CO and NO molecules in solid state, there is randomness even at 0 K due to their dipole moment hence entropy in such cases is not zero even at 0 K.

As the temperature is raised, the molecules begin to vibrate. The number of ways in which the vibrational energy can be distributed increases with increase in temperature and the entropy of the solid increases steadily as the temperature increases. At the melting point (m.p.) of a solid, there is a discontinuous jump in entropy because there are many more ways of arranging the molecules in the liquid than in the solid. An even greater jump in entropy is observed at the boiling point (b.p.) because molecules in the gas are free to occupy a more larger volume and randomness increases.

124. From the figure representing enthalpy change of various transition as indicated, a substance has maximum enthalpy when present in:



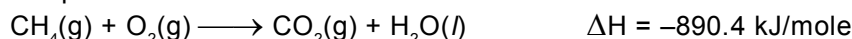
- (A) solid state (B) liquid state
(C) gaseous state (D) equal in all states
125. For the following reaction, $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
If at 0 K, ΔS of this reaction is $x \text{ cal mol}^{-1}$ then entropy of $\text{CO}_2(\text{g})$ at 0 K is :
(A) $-x \text{ cal}$ (B) $-2x \text{ cal}$ (C) $+x \text{ cal}$ (D) 0 cal
126. Which has the highest entropy per mol of the substance?
(A) H_2 at 25°C at 1 atm (B) H_2 at STP
(C) H_2 at 100 K at 1 atm (D) H_2 at 0 K at 1 atm

COMPREHENSION # 24

Paragraph for Questions Nos. 127 to 129

Enthalpy of reaction : It is used for the heat change accompanying any reaction. depending upon the nature of the reaction the enthalpy of the reaction is named accordingly

For example : In the reaction



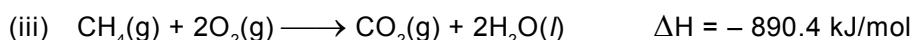
This reaction shown that 890.4 kJ of heat is produced when methane is completely burnt it is known as heat of combustion .

for example: In the reaction



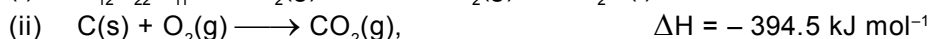
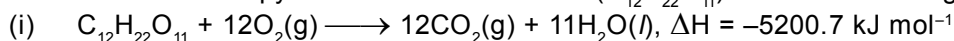
when $\text{CO}_2(\text{g})$ is formed from its elements i.e. from $\text{C}(\text{s})$ and $\text{O}_2(\text{g})$ 393.5 kJ of heat is produced and the process in heat of formation.

127. The enthalpy of formation of methane from the following data



- (A) -74.9 kJ/mole (B) 54.6 kJ/mole (C) 99.7 kJ/mole (D) -89.6 kJ/mole

128. Calculate the enthalpy of formation of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) from the following data:



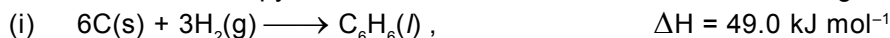
- (A) -10.3 kJ/mole

- (B) + 863.4 kJ/mole

- (C) -2677.1 kJ/mole

- (D) -4321.3 kJ/mole

129. Calculate the enthalpy of combustion of benzene from the following data:



- (A) + 463.6 kJ/mole

- (B) +32.4 kJ/mole

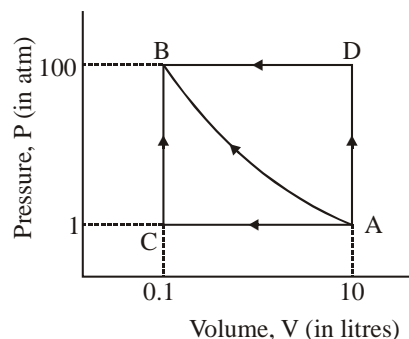
- (C) -1432.3 kJ/mole

- (D) -3242.2 kJ/mole

COMPREHENSION # 25

Paragraph for Questions Nos. 130 to 132

Assume perfect gas behaviour in the following isotherm AB. Take $C_v = \frac{3}{2} R$, temperature of the isotherm = 313 K



- 130.** Number of moles of gas in this system at the start is:
(A) 0.39 mol (B) 0.17 mol (C) 0.78 mol (D) 0.34 mol
- 131.** Work done on the gas along the isotherm AB is:
(A) -4.78 kJ (B) -8 kJ (C) +4.78 kJ (D) + 71 kJ
- 132.** ΔE (Change in internal energy) for path ACB or ADB is:
(A) 19.7 kJ (B) 0.00 kJ (C) 51.2 kJ (D) 3.0 kJ

AnswerKey

Qs.	Ans.	Qs.	Ans.
56	C	101	A
57	A	102	D
58	A	103	A
59	C	104	C
60	D	105	C
61	B	106	C
62	A	107	D
63	D	108	D
64	B	109	A
65	A	110	B
66	D	111	D
67	D	112	B
68	D	113	A
69	A	114	C
70	B	115	B
71	A	116	A
72	D	117	C
73	B	118	C
74	A	119	A
75	B	120	B
76	A	121	B
77	B	122	A
78	A	123	A
79	D	124	C
80	A	125	C
81	B	126	A
82	D	127	A
83	C	128	C
84	C	129	D
85	C	130	A
86	B	131	C
87	C	132	B
88	C		
89	D		
90	B		
91	D		
92	C		
93	C		
94	C		
95	B		
96	A		
97	B		
98	C		
99	C		
100	B		