Chemistry Spectrum

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JEE ADVANCED
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

From The Editor's Desk
CONCEPTUALISE CHEMISTRY

JEE
Final Touch

Fast Track Revision

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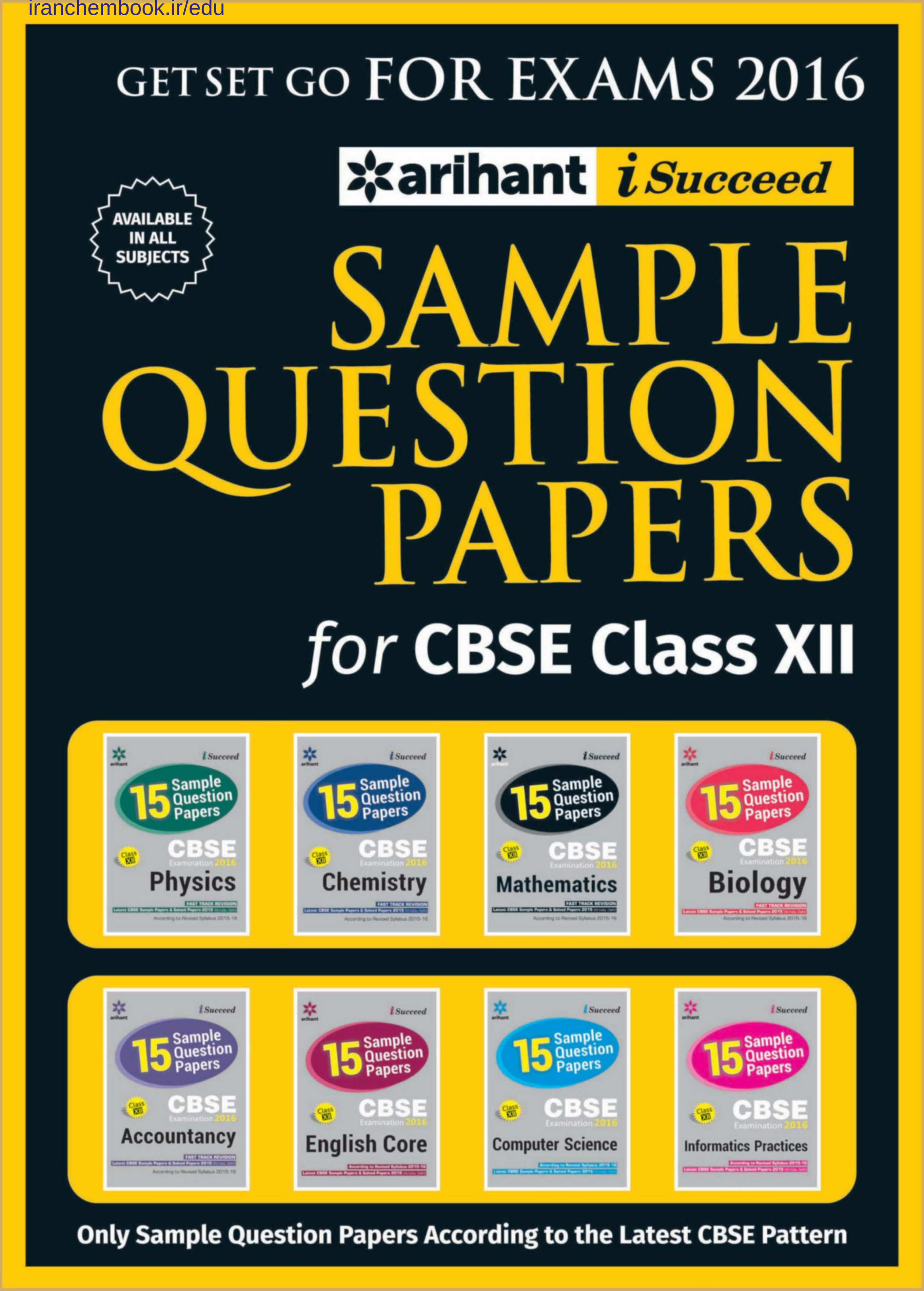

15 Sample Question Papers
CBSE Examination 2016
Physics
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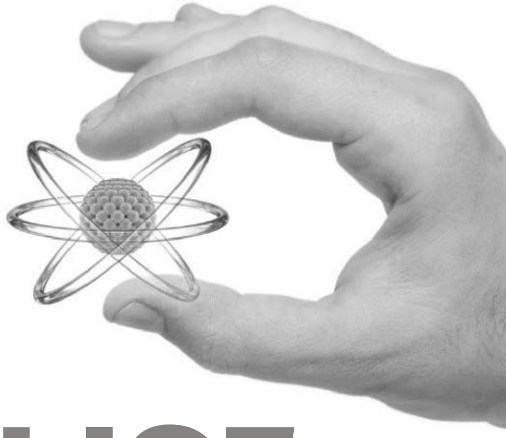


FROM THE EDITOR'S DESK

CONCEPTUALISE CHEMISTRY

Chemistry is the most dependable subject among all the three. It may be the most favourite for some and may be the scariest for others. Actually in my opinion some of the students have the aptitude of this subject while others do not. So those who have the aptitude of this subject like it most, while others develop a fear for this subject.

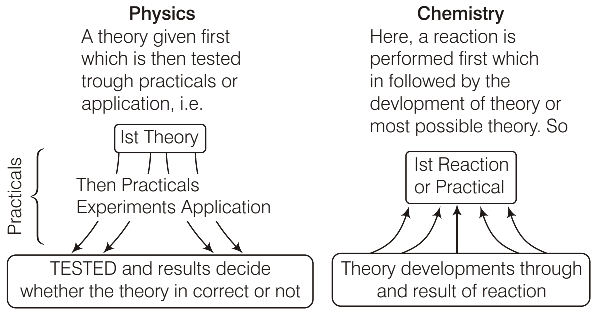
For me Chemistry is the mysterious subject. (Chemistry – che + mistry or **mystry**). Imagine nobody has seen electron till date but many of us has written books on it. Likewise nobody has seen interaction type between the particles during the reaction but the explanation or mechanisms of almost all reactions are there with us. Actually for that someone has to jump into the test tube while reaction is going on. So in a way it is a bit different and unique. Before discussing more about the nature of this subject it is better to understand its importance for JEE. As mentioned in the beginning it is the most dependable subject for JEE which simply indicates its importance. As far as my experience and analysis says **Physics and Maths are the two subjects on the basis of which the selection of an aspirant in IIT is determined. Chemistry on the other hand is responsible for the merit position of an aspirant.** This analysis is based on the fact that whenever a comparison is made between the marks of a high ranker and low ranker in IIT-JEE, the significant difference is visible only in the Chemistry marks, while the marks of Physics and Maths remain more or less same. Naturewise I consider this subject as exactly opposite to that of physics i.e. for me

← Physics   Chemistry →

Now you will say HOW? Or Why I consider so?

My answer for this How and Why is very clear and based upon following assumptions :

You can yourself observe the same i.e. in the case of physics theory is developed first followed by practicals or applications to verify it while in the case of chemistry practicals (reactions) occur first and later on the related theory is developed on the basis of its end results.



Thus, **the placement of both theory and practicals is opposite which in turn, make them opposite naturewise**. *This is the only reason why some students have a good command over :*

1. **Physics and Maths** with the fear of chemistry or
2. **Chemistry and Maths** with the fear of physics.

However, the students with equal or almost equal command over Physics and Chemistry are comparatively less. Naturewise one more interesting observation can be made about these subjects, i.e. as Physics involves verification of theory given through practicals or applications, hence the end results in the case of this subject are many and variable.

The more questions with marks like kyon or why, how etc., you apply, the more variability you can achieve. However, such a pattern is not applicable in chemistry. Here, the end result is one and that is certain, means it cannot be changed and we have to develop the theory in accordance with the end result.

That's why in this particular subject such type of questions are of lesser importance.

MANTRAS TO CAPTURE THE MYSTERIOUS CHEMISTRY

Now, here the compulsion is that the theory must be developed in accordance with the result we got, instead the generalised perception about acids written above. In more simple words, we can say that in chemistry, we have limitations i.e. the limitations of end results of the reactions and as these end results are certain (not changeable) hence, we have to think or develop our concept logically in accordance with the situation. That's why the theory in chemistry is not the 'certain theory' rather, it is the 'most probable theory'. Further as the end result may change with change in situations hence, one may found **'exceptions' to the theory** developed more frequently as compared to any other subject. So while going for chemistry remember!

1. There will be certain end result of any chemical reaction which limits our working arena technically.
2. The end result may change in accordance with situations, thus in turn give birth to so called **'exceptions'** in chemistry.
3. Most of the theories or rules covered in chemistry are results based and as nobody has seen interacting particles in a test tube hence, these theories or rules are considered under the **'most probable'** category.
4. In the purview of first three statements, we can conclude that the aptitude of chemistry involves explorations into the subject with very limited **'kyon'** or **'why'** or 'how' like punctuations.
5. Beside the above written aspects, language plays a very important role in tackling chemistry. A small twist in language changes the entire meaning of the question. So, nature wise a substantial control over language is required along with the aptitude to grip this subject properly.

   Keep only one thing in mind:

" It's the constant and determined effort that breaks down all resistance, sweeps away all obstacles"

Claude M. Bristol

Sharma

@CLASS XI SYLLABUS

JEE Final Touch

Fast Track Revision

Thermodynamics and Thermochemistry

ENTHALPY OF A REACTION AND CALORIMETRY

It is a branch of physical chemistry in which we study about the energy change associated with chemical reaction.

Enthalpy of a Reaction (H)

Mostly chemical reactions in the laboratory are carried out in open systems. The atmospheric pressure does not change during the reaction, so the reaction occurs at constant pressure. The heat released or absorbed during the reaction at constant pressure is known as **enthalpy of reaction**.

e.g. $H_2(g) + Cl_2(g)$ ¾ $2HCl(g)$; $H = 44$ kcal

Enthalpy of a reaction (H) = Sum of enthalpies of products (H_P) sum of enthalpies of reactants (H_R).

Standard Enthalpy of a Reaction ($H°$)

When enthalpy of a reaction is determined at 25°C temperature and 1 atm pressure, enthalpy of reaction is referred as **standard enthalpy of reaction**.

Exothermic and Endothermic Reactions

- The chemical reaction in which heat is evolved during the course of reaction, is known as **exothermic reaction**.
  e.g. $C(s) + O_2(g)$ ¾ $CO_2(g)$; $H = -393.0$ kJ
- The chemical reaction in which heat is absorbed during the course of reaction, is known as **endothermic reaction**.
  e.g. $2NH_3(g)$ ¾ $N_2(g) + 3H_2(g)$; $H = +92.3$ kJ

Flameless Heaters

These are used where cooking is difficult or impossible. Much of the development work in this area was done for military uses. In combat, lighting a fire is not advisable if you are trying to keep your location secret. These are also useful where electricity is not available.

Flameless heaters rely on an exothermic reaction to provide hot food. In a heatermeal products, the food is sealed inside a metal foil pouch and this is placed inside a plastic bag containing a heating pad made up of a mixture of magnesium and iron. To start the heating process, a little amount of water (~30 mL) is poured into the plastic bag. An exothermic reaction starts and the foil pouch containing the food gets hot. The heaters will heat 300 g of food or water to 80°C from room temperature in about 10 min.

Factors Affecting Enthalpy of a Reaction

1. **Physical state of reactants and products** Reactants having different allotropic forms or physical states have different enthalpies during course of their reactions. It is due to different allotropic forms are held by forces of different attraction strengths.
2. **Reaction conditions** At constant pressure, heat change associated with chemical reaction is equal to enthalpy change (H) while at constant volume it is equal to internal energy change (U).

   H and U are related as, $H = U + n_gRT$

   where, n_g = number of moles of gaseous products number of moles of gaseous reactants.

3. **Temperature** Values of H and U vary with temperature according to following Kirchhoff's equations,

$$H_2 \quad H_1 = C_p\,(T_2 \quad T_1) \text{ or } H_2 \quad H_1 = \int_{T_1}^{T_2} C_p\,dT$$

$$U_2 \quad U_1 = C_V\,(T_2 \quad T_1) \text{ or } U_2 \quad U_1 = \int_{T_1}^{T_2} C_V\,dT$$

4. **Amount of reactant** H and U depend upon amount of reactant, e.g. 20 g of carbon produces more heat than 2.0 g of carbon on combustion.

Calculation of U and H values by a Calorimeter

(a) **For gaseous reactions** Reactions involving gases are carried out in a bomb calorimeter, as the reaction needs to be carried out at constant volume.

U value can be calculated as,

$$U = \quad \text{(Heat absorbed by bomb calorimeter)}$$

(b) **For reaction in solution** Reaction involving solution are carried out at constant pressure inside a coffee-cup calorimeter.

$$_rH = \text{Heat absorbed/released by calorimeter}$$
$$+ \text{ heat absorbed/released by solution.}$$
$$= (mc \quad T) \text{ calorimeter} + (mc \quad T) \text{ solution}$$

Here, c = specific heat capacity.

Energetics of Food

- A calorimeter is a piece of equipment designed to measure the energy released or absorbed during a chemical reaction or phase change.
- With the help of food calorimetry, we can determine the number of calories per gram of food.
- People who check nutrition labels to make decisions about which foods to eat and which to avoid often base on the number of calories per serving.
- A calorie is a unit of energy as joule, however calorie is commonly used for a unit of food energy.

Best Practice SHOTS

1. For an endothermic reaction, if H is given in kJ/mol. The minimum value for energy of activation will be

(a) less than H *(b)* zero
(c) more than H *(d)* equal to H

Hint For an endothermic reaction products are at higher energy level than reactants.

2. For the reaction,

$$C_2H_5OH(l) + 3O_2(g) \text{ ¾ } 2CO_2(g) + 3H_2O(l)$$

The correct option is

(a) $H = U \quad RT$ *(b)* $H = U + RT$
(c) $H = U + 2RT$ *(d)* $H = U \quad 2RT$

3. C_p for a reaction is given by $2.0 + 0.2\ T$ cal/°C, its enthalpy of reaction at 10 K is 14.2 kcal. Enthalpy of reaction at 100 K will be (in kcal)

(a) 15.37 *(b)* 14.09
(c) 13.21 *(d)* 7.80

Hint $H_2 \quad H_1 = \int_{T_1}^{T_2} C_p\,dT$

4. Molar heat capacity of water in equilibrium with the ice at constant pressure is

(a) zero *(b)*
(c) 40.45 kJ mol ^{1} *(d)* 57.6 kJ mol ^{1}

5. The reaction for which the difference (H U) would be minimum among the following reactions (at same temperature for all) is

(a) $2KClO_3(g)$ ¾ $2KCl(s) + 3O_2(g)$
(b) $N_2(g) + 3H_2(g)$ ¾ $2NH_3(g)$
(c) $H_2(g) + I_2(g)$ ¾ $2HI(g)$
(d) $2SO_2(g) + O_2(g)$ ¾ $2SO_3(g)$

6. Find the wrong statement among the following options, the heat of reaction depends on

(a) the temperature at which the reaction is carried out
(b) the manner by which the reaction is carried out
(c) physical state of reactants and products
(d) whether the reaction is carried out at constant pressure or at constant volume

7. For the reaction,

$$C + O_2 \text{ ¾ } CO_2; \quad H = \quad 393\,\text{kJ}$$

and $2Zn + O_2$ ¾ $2ZnO; \quad H = \quad 412$ kJ

Which one is the correct statement?

(a) Carbon can reduce ZnO to Zn
(b) Oxidation of carbon is not feasible
(c) Oxidation of carbon and zinc both takes place
(d) Oxidation of zinc is not feasible

Hint Since, H for Zn ¾ ZnO is more negative, indicates that on coupling both the reactions, carbon can reduce ZnO to Zn. Because on reversing the equation for zinc, the value of H becomes positive. This indicates, ZnO is less stable and can be reduced to Zn by carbon.

8. (H U) for the formation of CO from its elements at 298K is (Given, R = 8.31JK ^{1}mol ^{1})

(a) 1238.78 J mol ^{1} *(b)* 1238.78 J mol ^{1}
(c) 2477.57 J mol ^{1} *(d)* 2477.57 J mol ^{1}

DIFFERENT STANDARD ENTHALPY CHANGE AND LAWS OF THERMOCHEMISTRY

Different Standard Enthalpy Change

The following table represents the name and definition of different types of standard enthalpy change.

Definition of different types of standard enthalpy change	Example
Enthalpy of formation ($_{f}H°$) The enthalpy change for the formation of one mole of a compound from its elements in their most stable state.	$H_2(g) + \frac{1}{2}O_2(g)$ ¾ $H_2O(l)$; $_{f}H° = \quad 285.8\ \text{kJ mol}^{1}$ $_{f}H°$ value of an element in its most stable state is taken as 0.
Enthalpy of combustion ($_{C}H°$) The amount of heat evolved or absorbed when one mole of the substance is completely burnt in oxygen or air.	$C_6H_{12}O_6(g) + 6O_2(g)$ ¾ $6CO_2(g) + 6H_2O(l)$; $_{C}H° = [(6 \quad H°_{f(CO_2)}) + (6 \quad H°_{f(H_2O)})]$ $[\ H°_{f(C_6H_{12}O_6)} + (6 \quad H°_{f(O_2)})]$ $_{C}H° = \quad 2802\ \text{kJ mol}^{1}$ The heat produced due to the combustion of 1g of a fuel is called **calorific value.**
Enthalpy of fusion ($_{fus}H°$) The enthalpy change when one mole of solid substance changes into its liquid form at constant temperature.	$H_2O(s)$ ¾ $H_2O(l)$; $_{fus}H° = 6\ \text{kJ mol}^{1}$ The temperature at which a solid is converted into liquid is called its **melting point**.
Enthalpy of vaporisation ($_{vap}H°$) The enthalpy change when one mole of liquid substance changes into its vapour form.	$H_2O(l)$ ¾ $H_2O(g)$; $_{vap}H° = 40.8\ \text{kJ mol}^{1}$
Enthalpy of sublimation ($_{sub}H°$) The enthalpy change when one mole of solid substance changes into its vapour form.	$H_2O(s)$ ¾ $H_2O(g)$; $_{sub}H° = 51.1\ \text{kJ mol}^{1}$ $_{sub}H° = \ _{fus}H° + \ _{vap}H°$
Enthalpy of atomisation ($_{atom}H°$) Enthalpy change when one mole of a substance is broken down into its constituent isolated atoms in gaseous state.	$H_2(g)$ ¾ $2H(g)$; $_{atom}H° = 43.5\ \text{kJ mol}^{1}$
Enthalpy of neutralisation ($_{n}H°$) Enthalpy change when 1 mole of water is formed by acid-base neutralisation.	$H^+(aq) + \bar{O}H(aq)$ ¾ $H_2O(1)$; $_{n}H° = \quad 57.1\ \text{kJ}$
Bond dissociation enthalpy ($_{bond}H°$) Enthalpy change when all the bonds present in one mole of a compound are broken in gaseous state.	$CH_4(g)$ ¾ $C(g) + 4H(g)$; $_{atom}H° = 1665\ \text{kJ mol}^{1}$ $_{r}H° = \quad _{bond}H°$ (reactants) $_{bond}H°$ (products)
Enthalpy of solution ($_{sol}H°$) Enthalpy change when one mole of a solute is dissolved in excess of solvent.	$NaCl(g)$ ¾ $Na^+(aq) + Cl^-(aq)$; $_{sol}H° = 4\ \text{kJ mol}^{1}$ $_{sol}H° = \ _{lattice}H° + \ _{hyd}H°$
Lattice enthalpy ($_{lattice}H°$) Enthalpy change when one mole of an ionic compound dissociates in gaseous state.	$NaCl\ (g)$ ¾ $Na^+(g) + Cl\ \ (g)$; $_{lattice}H° = 788\ \text{kJ mol}^{1}$

CHEMISTRY CONCENTRATE

PROBLEMS RELATED TO ENTHALPY

- First of all, write down all the balanced chemical reactions including their enthalpy change value.
- Mark these reactions in terms of equation number.
- Write down the chemical reaction for which we have to find out enthalpy change value.
- Arrange the given equation in such a manner that we could get the required equation.
- For this purpose, we can apply operation such as addition or subtraction of equations and multiplying or dividing by an integer to the equation.
- Same operations should be applied for given enthalpy change values as well.
- Finally, we get the required enthalpy change value.

REMEMBER

Except bond dissociation, enthalpy change for any other process is given as,

Enthalpy change
= Sum of enthalpies for all products   sum of enthalpies for all reactants.

But for bond dissociation,

Enthalpy change
= Sum of enthalpies of all reactants   sum of enthalpies of all products.

Laws of Thermochemistry

Lavoisier and Laplace's Law

The enthalpy of decomposition of a compound is numerically equal to the enthalpy of formation of that compound with opposite sign,

e.g. $A + B$ ¾ C; $\quad H = x$

C ¾ $A + B$; $\quad H = \quad x$

Hess's Law of Constant Heat Summation

Enthalpy change for a reaction is same whether the reaction is carried out in one step or in several steps.

e.g. $C(g) + O_2(g)$ ¾ $CO_2(g)$; $\ _{r}H$

$C(s) + \frac{1}{2}O_2(g)$ ¾ $CO(g)$; $\ _{r}H_1$

$CO(g) + \frac{1}{2}O_2(g)$ ¾ $CO_2(g)$; $\ _{r}H_2$

According the Hess's law,

$$_{r}H = \ _{r}H_1 + \ _{r}H_2$$

Best Practice SHOTS

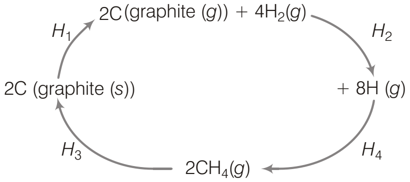
9. When 1g of carbon-atom is converted to 1g molecule of CO_2, the heat is same

(a) irrespective of whether the volume is kept constant or pressure is kept constant
(b) irrespective of the temperature at which the reaction is carried out
(c) where carbon is in the form of graphite or diamond
(d) None of the above

10. For the reactions, $H_2(g) + Cl_2(g)$ ¾ $2HCl(g) + x_1$ kJ and $2HCl(g)$ ¾ $H_2(g) + Cl_2(g) \quad x_2$ kJ, the correct statement is

(a) x_1 and x_2 are numerically equal
(b) $x_1 = 4x_2$
(c) $x_1 \quad x_2 > 0$
(d) $x_1 \quad x_2 < 0$

11. From the figure given below



The values of

heat of formation of CH_4, heat of sublimation of graphite and heat of dissociation of H_2, (in terms of H_1, H_2, H_3 and H_4) respectively are (i.e. correct order is)

(a) $\frac{H_2}{4}, \frac{H_1}{2}, \frac{H_1 + \quad H_2 + \quad H_4}{2}$
(b) $\frac{H_1 + \quad H_2 + \quad H_4}{2}, \frac{H_1}{2}, \frac{H_2}{4}$
(c) $\frac{H_3}{4}, \frac{H_2 + \quad H_1}{2}, \frac{H_4}{2}$
(d) $\frac{H_2}{2}, \frac{H_3 + \quad H_1}{2}, \frac{H_4}{4}$

12. $NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g); \quad H_1$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad H_2$

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g); \quad H_3$

The heat of formation of $NCl_3(g)$ in terms of H_1, H_2, and H_3 will be

(a) $H_f = \quad H_1 \quad \frac{H_2}{2} \quad \frac{3}{2} \times H_3$
(b) $H_f = H_1 + \frac{H_2}{2} \quad \frac{3}{2} \times H_3$
(c) $H_f = H_1 \quad \frac{H_2}{2} + \frac{3}{2} \cdot \quad H_3$
(d) All of the above options give the same result

13. The standard enthalpy of formation (H_f°) at 298K for methane (CH_4) is 74.8 kJ mol ^{1}.

The additional information required to find the average bond energy of C ¾ H bond formation would be

(a) first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(b) the dissociation energy of $H_2(g)$
(c) latent heat of vaporisation of methane
(d) the dissociation energy of $H_2(g)$ and enthalpy of sublimation of carbon

14. The latent heat of vaporisation of water is 10.5 kcal mol ^{1} at 25°C and standard heat of formation of liquid water is 68.3 kcal.

The enthalpy change of the reaction,

$$H_2(g) + \frac{1}{2}O_2(g) \text{ ¾ } \quad H_2O(g) \text{ is,}$$

(a) 57.8 kcal	*(b)* 78.8 kcal
(c) + 57.8 kcal	*(d)* + 78.8 kcal

15. A cylinder of gas supplied by a company is assumed to contain 14 kg of butane. If normal family requires 20,000 kJ of energy per day for cooking, how long will the cylinder last?

(Given, heat of combustion of butane = 2658 kJ)

(a) 23 days	*(b)* 32 days
(c) 50 days	*(d)* 42 days

Hint Number of days cylinder works

$$= \frac{\text{Energy provided by } 14 \quad 10^3\text{g gas}}{\text{Energy required per day}}$$

16. Bond dissociation energy of XX, XY and Y_2 (all are diatomic) are in the ratio of 1 :1: 0.5 respectively and H_f of XY is 200 kJmol ^{1}, then bond dissociation energy for X_2 is

(a) 880 kJ mol ^{1}	*(b)* 800 kJ mol ^{1}
(c) 200 kJ mol ^{1}	*(d)* 400 kJ mol ^{1}

Hint Required relation is $\frac{1}{2}X_2 + \frac{1}{2}Y_2$ ¾ $\quad XY$

$$H_r = [BE\frac{1}{2}(X_2) + BE\frac{1}{2}(Y_2) \quad BE(XY)]$$

$$H_r = 200 \text{ kJ mol } ^{1}$$

17. For enthalpy changes,

$Cl_2(g)$ ¾ $2Cl(g)$; 242.3kJ mol ^{1}
$I_2(g)$ ¾ $2I(g)$; 151.0 kJ mol ^{1}
$ICl(g)$ ¾ $I(g) + Cl(g)$; 211.3 kJ mol ^{1}
$I_2(s)$ ¾ $I_2(g)$; 62.76 kJ mol ^{1}

If standard states for iodine and chlorine are I_2 (*s*) and Cl_2 (*g*), the H_f° for ICl(*g*) is

(*a*) 14.6 kJ mol ^{1} (*b*) 16.8 kJ mol ^{1}
(*c*) + 16.7 kJ mol ^{1} (*d*) + 14.6 kJ mol ^{1}

18. When 1.4 g of iron combines with sulphur, 1.9 kJ of heat comes out. Thus, standard enthalpy of formation of FeS is

(*a*) 19 kJ (*b*) 76.0 kJ (*c*) 3.8 kJ (*d*) zero

19. The enthalpy of formation of $C_2H_5OH(l)$ is 66 kcal/mol. The enthalpy of combustion of $CH_3OCH_3(l)$ is 348 kcal/mol. Find, *H* for isomerisation of ethanol to methoxymethane (CH_3OCH_3).

Given, H_f° for $CO_2(g)$ = 94 kcal/mol

H_f° for $H_2O(l)$ = 68 kcal/mol.

(The whole reaction occurs under standard conditions).

(*a*) 66 kcal/mol (*b*) 22 kcal/mol
(*c*) 44 kcal/mol (*d*) 88 kcal/mol

20. Sublimation energy for $I_2(s)$ is 57.3 kJ/mol and enthalpy of fusion is 15.5 kJ/mol. The enthalpy of vaporisation for I_2 is

(*a*) 41.8 kJ/mol (*b*) 41.8 kJ/mol
(*c*) 72.8 kJ/mol (*d*) 72.8 kJ/mol

Hint $H_{sub} = H_{fus} + H_{vap}$

ENTROPY (*S*) AND GIBBS FREE ENERGY (*G*)

Entropy (*S*)

- A thermodynamic quantity that provides a quantitative measure of how much energy is spread out when something happens during a chemical reaction.

or

- A thermodynamic property that measures the extent of molecular disorder or randomness.

It is a state function, used to define the second law of thermodynamics.

Gibbs Free Energy (*G*)

- It is a state function. It is defined as hypothetical infinitesimal energy which is used up during a spontaneous process.

or

- It is defined as the maximum amount of energy available to a system during a process that can be converted into useful work.

Spontaneity of a Chemical Reaction

The spontaneity of a reaction depends on *H*, *S* and *T*, is given by the following table:

H	*S*	*G* = *H* *T* *S*	Reaction spontaneity
Exothermic ( )	+		Spontaneous at all temperatures.
			Spontaneous at low temperatures.
		+	Non-spontaneous at high temperatures.
Endothermic (+)	+	+	Non-spontaneous at low temperatures.
	+		Spontaneous at high temperatures.
		+	Non-spontaneous at all temperatures.
T *S* = *H*		0	Equilibrium

Formulae Related to Entropy and Gibbs Free Energy

Entropy

- At constant pressure, when temperature changes,

$$S = 2.303\, nC_p \log \frac{T_2}{T_1}$$

- At constant volume, when temperature changes,

$$S = 2.303\, nC_V \log \frac{T_2}{T_1}$$

- At constant temperature, when volume changes,

$$S = 2.303\, nR \log \frac{V_2}{T_1}$$

- At constant volume, when both temperature and pressure change,

$$S = 2.303 \left(nC_V \log \frac{T_2}{T_1} + nR \log \frac{p_1}{p_2} \right)$$

- At constant pressure, when both temperature and volume change,

$$S = 2.303 \left(nC_p \log \frac{T_2}{T_1} \quad nR \log \frac{V_1}{V_2} \right)$$

- When phase transition occur during the process, $S = \frac{H}{T}$

For solid to liquid phase change, $H = H_{fus}$
For liquid to gas phase change, $H = H_{vap}$
For solid to gas phase change, $H = H_{sub}$

Gibbs Free Energy

$$G = H \quad T \quad S$$

$$G = W = 2.303 RT \log \frac{V_2}{V_1}$$

$$G = G^\circ + 2.303\, RT \log Q$$

At equilibrium, $G^\circ = 2.303\, RT \log K$

Best Practice SHOTS

21. If, PbO_2 ¾ PbO; G at 298 K < 0 and SnO_2 ¾ SnO; G at 298 K > 0. Then, most probable oxidation states for Pb and Sn are

(a) Pb^{4+} ,Sn^{4+} (b) Pb^{2+}, Sn^{4+}
(c) Pb^{2+}, Sn^{2+} (d) Pb^{4+}, Sn^{2+}

Hint Given,
(i) G for the formation of Pb^{2+} is negative means Pb^{2+} is more stable than Pb^{4+}.
(ii) G for the formation of Sn^{2+} is positive means it is less stable.

22. For a reaction, $H_2O(s) \rightleftharpoons H_2O(l)$ at 0°C temperature and normal pressure, the correct choice is

(a) $H < T\ S$ (b) $H = \ G$
(c) $H = T\ S$ (d) $S = 0$

Hint At equilibrium,

$$G = 0 \text{ means}$$
$$H = T\ S; \qquad (\because\ G = \ H \quad T\ S)$$

23. When an egg is boiled, its entropy

(a) increases (b) decreases
(c) shows no change (d) becomes zero

24. Silane (SiH_4) burns in air as,

$$SiH_4(s) + 2O_2(g) ¾ \quad SiO_2(s) + 2H_2O(l)$$

The standard Gibbs energies of formation of $SiH_4(g)$, $SiO_2(s)$ and $H_2O(l)$ are + 52.3, – 805.0 and – 228.6 kJ mol ^{1} respectively. Calculate Gibbs free energy change in kJ for the reaction.

(a) – 1314.5 (b) – 1472.3 (c) – 1582.3 (d) – 1272.8

25. In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser, the reaction is,

$$CH_3OH(l) + \frac{3}{2}O_2(g) ¾ \quad CO_2(g) + 2H_2O(l)$$

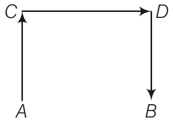
At 298 K, G° of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are 166.2, 237.2 and 394.4 kJ mol ^{1} respectively.

If standard enthalpy of combustion of methanol is 726 kJ mol ^{1}, efficiency of the fuel cell will be

(a) 70% (b) 80% (c) 90% (d) 97%

Hint Efficiency (%) = $\frac{G}{H}$ 100

26. The direct conversion of a substance is difficult from *A* to *B*. Hence, the process is carried out as follows:



Given, S (A C) = 50 units, S (C D) = 30 units and S (B D) = 20 units

Then, net entropy for the process from *A* to *B* is (in true of number of units)

(a) 60 (b) +60
(c) 100 (d) +100

Hint Net entropy change (S) = $S_{A\ C} + S_{C\ D} + S_{D\ B}$
$= S_{A\ C} + S_{C\ D} \quad S_{B\ D}$

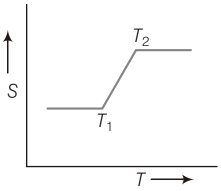
27. For a cell reaction, (at 25°C)
$Zn(s) + Cu^{2+}(aq)$ — $Zn^{2+}(aq) + Cu(s)$, the value of emf is 1 V.

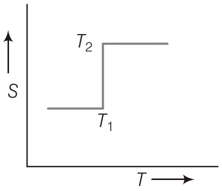
If enthalpy of reaction is 197.5 kJ/mol, the change in standard molar entropy will be (in JK ^{1}mol ^{1})

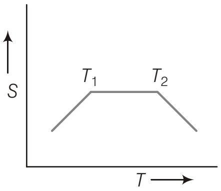
(a) 11.5 (b) 15.1
(c) 11.5 (d) 15.1

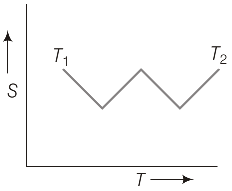
Hint $G° = \ nFE°$ also $G° = \ H° \quad T\ S°$

28. T_1 and T_2 are freezing and melting points of a substance, which of the following graphs represents correctly about the variation of S with temperature?

(a)


(b)


(c)


(d)


Hint T_1 and T_2 will be same for freezing and melting point.

Answers

1. (c) **2.** (a) **3.** (c) **4.** (b) **5.** (b) **6.** (b) **7.** (a) **8.** (b) **9.** (a) **10.** (a)
11. (b) **12.** (a) **13.** (d) **14.** (a) **15.** (b) **16.** (b) **17.** (c) **18.** (b) **19.** (b) **20.** (a)
21. (b) **22.** (c) **23.** (a) **24.** (a) **25.** (d) **26.** (b) **27.** (b) **28.** (b)

MASTER STROKE

1. Heat of neutralisation for four acids *A*, *B*, *C* and *D* are 13.7, 9.4, 11.2 and 12.4 kcal respectively, when they are neutralised by a common base. The order of their acidic strength is

(a) $A > B > C > D$ (b) $D > C > B > A$
(c) $A > D > C > B$ (d) $B > C > D > A$

Hint Lower be the heat of neutralisation more be the dissociation energy. Thus, weaker be the acid.

2. A solution of 250 mL of 2M KOH is added to 250 mL of 2 M HCl and shaken. The rise in temperature T_1 is noted. The experiment again repeated, taking 500 mL of each solution, the rise in temperature T_2 is noted. Assume all the heat is taken up by the solution in both the cases.

The relation between T_1 and T_2 is

(a) $T_1 = T_2$ (b) $2T_1 = T_2$
(c) $T_1 = 2T_2$ (d) $T_1 = 4T_2$

Hint The heat evolved in first case is twice as compared with second case but since, volume also becomes double, the temperature in both the cases remain same.

3. The ionisation energy of solid NaCl is 180 kcal per mol. The dissolution of the solid in water in form of ions is endothermic to the extent of 1 kcal per mol. If the solvation energies of Na^+ and Cl ions are in the ratio of 6 : 5. Then, enthalpy of hydration for sodium ions per mol is

(a) 82.6 kcal (b) 85.6 kcal
(c) 97.6 kcal (d) 100 kcal

Hint H solution $= H_i + H_h$.

Given, H solution $= 1$ and $H_i = 180$.

$$1 = H_i + H_h$$

$$1 = 180 + H_h$$

$$H_h = 179 = H_h(Na^+) + H_h(Cl\ )$$

∵ Na^+ and Cl has ratio of solvation energy = 5 : 6

$$H_h = \frac{6}{11}(Na^+) + \frac{5}{11}(Cl\ ) = 179$$

$$H_h(Na^+) = -\frac{6\quad 179}{11} = \quad 97.6 \text{ kcal}$$

4. The average molar heat capacities of ice and water are 37.6 and 75.2 J mol ^{1}K ^{1}respectively. Its enthalpy of fusion is 6.02 kJ mol ^{1}. The amount of heat required to raise the temperature of 10 g of water from 10°C to 10°C is equal to

(a) 2376 J (b) 4572 J
(c) 1129 J (d) 3971 J

Hint Required steps are:

(i) 10 g of ice at 10°C 10 g of ice at 0°C

(ii) 10 g of ice at 0°C 10 g of water at 0°C
(Transformation state)

(iii) 10 g of water at 0°C 10 g of water at10°C.

Thus, heat required mc *t* + mL + mc *t*

5. Which of the following reactions is said to be enthalpy driven?

(a) Endothermic reaction with positive entropy change and high temperature
(b) Endothermic reaction with negative entropy change and low temperature
(c) Exothermic reaction with the entropy change and high temperature
(d) Exothermic reaction with negative entropy change and low temperature

6. The standard heat of combustion of Al is 837.8 kJ mol ^{1} at 25°C. If Al reacts with O_2 at 25°C, which of the following releases 250 kJ (approx.) of heat?

(a) The reaction of 0.625 mole of Al
(b) The reaction of 0.625 mole of Al_2O_3
(c) The reaction of 0.312 mole O of Al
(d) The reaction of 0.150 mole of Al_2O_3

7. Two moles of an ideal gas undergoes expansion under isothermal reversible condition from 5 to 50L at 27°C. The entropy change associated with this process is $[R = 8.3 \text{ J}]$

(a) 10 JK ^{1} (b) 16.0 JK ^{1}
(c) 38.2 JK ^{1} (d) 19.1 JK ^{1}

8. Given, $S(s) + \frac{3}{2}O_2(g)$ ¾ $SO_3(g) + 2x$ kcal

and $SO_2(g) + \frac{1}{2}O_2(g)$ ¾ $SO_3(g) + y$ kcal

Find the value of H_f° for SO_2

(a) $x \quad 2y$ (b) $y \quad 2x$
(c) $x + 2y$ (d) $\frac{2x}{y}$

9. Determine the enthalpy of the reaction,

$$C_3H_8(g) + H_2(g) \text{ ¾ } C_2H_6(g) + CH_4(g)$$

at 25°C, using the given heat of combustion values under standard conditions.

Compound	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C (graphite)
H° (kJ/mol)	285.0	890.0	1560.0	393.0

The standard heat of formation of $C_3H_8(g)$ is 103 kJ mol ^{1}.

(a) 49 kJ (b) 60 kJ
(c) 50 kJ (d) 55 kJ

10. Compute the heat of formation of liquid methyl alcohol in kJmol ^{1}, using the following data. Heat of vaporisation of liquid methyl alcohol = 38 kJ mol ^{1}. Heat of formation of gaseous atoms from the elements in their standard states,

H = 218kJ mol ^{1}, C = 715 kJ mol ^{1}
O = 249 kJ mol ^{1}

Average bond energies,

C ¾ H = 415 kJ mol ^{1}
C ¾ O = 356 kJ mol ^{1}
O ¾ H = 463 kJ mol ^{1}

(a) 274 (b) 266
(c) 220 (d) 277

11. Silane (SiH_4) burns in the air as

$$SiH_4(g) + 2O_2(g) \text{ ¾ } SiO_2(s) + 2H_2O(l)$$

The standard Gibbs energies of formation of $SiH_4(g)$, $SiO_2(s)$ and $H_2O(l)$ are +52.3, 805.0 and 228.6 kJ mol ^{1} respectively Calculate Gibbs energy change for the reaction.

(a) 1314.5 kJ (b) 1314.5 kJ (c) 895.07 kJ (d) 905.4 kJ

12. Match the following columns.

Column I		Column II	
A.	Spontaneous process	p.	*H* = ve
B.	Heat flow from high temperature of system to low temperature of surrounding	q.	*G* = +ve
C.	Exergonic process	r.	$_{total}S$ = + ve
D.	Increase in randomness of system by heating	s.	*G* = ve

Codes

	A	B	C	D
(a)	p	q,r	p,q	s,p
(b)	p,r	q,s	p	r,q
(c)	r,s	p,r,s	q	q,r
(d)	s,p	r,s	q	p

Answers

1. (c) 2. (a) 3. (c) 4. (d) 5. (d) 6. (d) 7. (c) 8. (b) 9. (d) 10. (b)
11. (a) 12. (c)

Equilibrium

LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Chemical equilibrium is a state of reversible reactions in which the concentrations of reactants and products do not change with time.

Law of Chemical Equilibrium (or Law of Mass Action)

According to this law, the rate at which a substance reacts is directly proportional to its active mass raised to the power of its stoichiometric coefficient. For a chemical reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$$R_f = K_f\,[A]^a\,[B]^b$$

$$R_b = K_b\,[C]^c\,[D]^d$$

At equilibrium, $R_f = R_b$

Formulae for equilibrium Constant in Terms of Different Quantities and Different Conditions

General reaction, $aA + bB \rightleftharpoons cC + dD$

	Quantity	Equilibrium constant
1.	Concentration	$K_C = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$
2.	Partial pressure	$K_p = \dfrac{(p_C^c)(p_D^d)}{(p_A^a)(p_B^b)} = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}(RT)^{\Delta n_g}$ $= K_C\,(RT)^{\Delta n_g}$
3.	Active mass	$K_a = \dfrac{[a_C]^C\,[a_D]^d}{[a_A]^a\,[a_B]^b} = \dfrac{(f_C)^c\,(f_D)^d}{(f_A)^a\,(f_B)^b} \times \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ $= K_f \times K_C$
4.	Mole fraction	$K_x = \dfrac{[\chi_C]^c\,[\chi_D]^d}{[\chi_A]^a\,[\chi_B]^b}$

General reaction, $A \rightleftharpoons B$ equilibrium constant

	Condition	Equilibrium constant
1.	$B \rightleftharpoons A$	$K^{-1} = \dfrac{1}{K}$
2.	$mA \rightleftharpoons mB$	$K' = (K)^m$
3.	$\dfrac{A}{m} \rightleftharpoons \dfrac{B}{m}$	$K'' = (K)^{1/m}$
4.	When temperature (T) is given	$\log K = -\dfrac{\Delta H°}{2.303RT} + \dfrac{\Delta S°}{R}$
5.	When temperature changes from T_1 to T_2	$\log\dfrac{K_{C_1}}{K_{C_2}} = \dfrac{\Delta H°}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$ $\log\dfrac{K_{p_1}}{K_{p_2}} = \dfrac{\Delta H°}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

Case I When $\Delta H° = 0$, $K_1 = K_2$, equilibrium constant (K) is independent from temperature (T).

Case II When $\Delta H° < 0$, (endothermic),
$K_2 > K_1$, K increases with increase in temperature.

Case III When $\Delta H° < 0$, (exothermic),
$K_2 < K_1$, K decreases with increase in temperature.

- Δn_g = Moles of gaseous products − moles of gaseous reactants.
- f = activity coefficient, for dilute solutions, $f = 1$
- For heterogeneous system, concentration of solid reactants or solid product is taken to be unity.
- If $\Delta n_g = 0$, $K_p = K_C$
  $\Delta n_g > 0$, $K_p > K_C$
  $\Delta n_g < 0$, $K_p < K_C$

Units of Equilibrium Constant K

$$K_p = (\text{atm})^{\Delta n};\ K_C = (\text{mol/L})^{\Delta n}$$

$$K_x = \text{unitless};\ K_a = (\text{mol/L})^{\Delta n}$$

Characteristics of Equilibrium Constant (K_p and K_C)

- K has a definite value for a given reaction at a particular temperature and it does not influence by any other factors except temperature.
- It is independent of initial concentration of reactants and products.
- The value of K remains same whether the equilibrium is achieved in forward or backward direction.

Based on the state of the reactants and products at equilibrium, chemical reactions are divided into two types:

Homogeneous Equilibria

All the reactants and products are in same phase (either gas or liquid).

Heterogeneous Equilibria

The reactants and products are in different phases at equilibrium.

{JEE FINAL TOUCH}

Procedure to find number of moles, mole fractions and *K* values at equilibrium

.	Homogeneous equilibria			Heterogeneous equilibria		
	$H_2(g)$ +	$I_2(g) \rightleftharpoons$	$2HI(g)$	$NH_4CO_2NH_2(s) \rightleftharpoons$	$2NH_3(g)$ +	$CO_2(g)$
Initial moles	a	b	0	1	0	0
Equilibrium moles	$(a-x)$	$(b-x)$	$2x$		$2x$	x
Total moles at equilibrium		$(a+b)$			$3x$	
Active masses	$\frac{a}{V}$	$\frac{b}{V}$				
Mole fraction	$\left(\frac{a-x}{a+b}\right)$	$\left(\frac{b-x}{a+b}\right)$	$\left(\frac{2x}{a+b}\right)$		$\frac{2}{3}$	$\frac{1}{3}$
Partial pressure	$p\left(\frac{a-x}{a+b}\right)$	$p\left(\frac{b-x}{a+b}\right)$	$p\left(\frac{2x}{a+b}\right)$		$\frac{2p}{3}$	$\frac{p}{3}$
K_C	$\frac{4x^2}{(a-x)(b-x)}$				$K_C = 4x^3$	
K_p	$\frac{4x^2}{(a-x)(b-x)}$				$K_p = \frac{4p^3}{27}$	

Note The active mass or concentration or partial pressure of pure solid, pure liquid and solvents are taken as unity(1), hence, they do not appear in rate equation.

Best Practice SHOTS

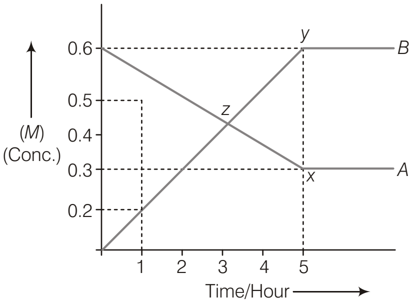
1. The equilibrium constant K_p, for the reaction, $A \rightleftharpoons 2B$, is related to degree of dissociation (α) of A and total pressure p as

(a) $\frac{4\alpha^2 p}{1-\alpha^2}$ (b) $\frac{4\alpha^2 p}{1-\alpha}$

(c) $\frac{4\alpha^2 p^2}{1-\alpha^2}$ (d) $\frac{4\alpha^2 p^2}{1-\alpha}$

2. Progress of the reaction, $A \rightleftharpoons nB$, with respect to time is shown below.

The stoichiometric coefficient of product B and value of equilibrium constant (K_C) respectively.



(a) 2 and 1.2 (b) 2 and 2

(c) 4 and 1.2 (d) 2 and 4

Hint (i) Concentration of A changes during 1h to 5h

$$= 0.5 \text{ to } 0.3 = 0.2 \text{ M}$$

Concentration of B changes during 1h to 5h

$$= 0.2 \text{ to } 0.6 = 0.4 \text{ M}$$

Thus,

$$\Delta[A] = 0.2 \text{ M}, \Delta[B] = 0.4 \text{ M}$$

Hence, $n = 2$

Means $A \rightarrow 2B$

(ii) At equilibrium, $[A] = 0.3$ M

$[B] = 0.6$ M

$$\therefore \quad K_C = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{(0.3)} = 1.2$$

Note Parallel lines with respect to x-axis at points x and y, show the equilibrium position of A and B respectively.

3. For the reactions,

$$A \rightleftharpoons B, K_1 = 2$$
$$B \rightleftharpoons C, K_2 = 4$$

and $$C \rightleftharpoons D, K_3 = 3$$

Then, for the reaction, $A \rightleftharpoons D$, under similar conditions, the value of equilibrium constant (K_{eq}) will be

(a) 6 (b) 12 (c) 24 (d) 48

Hint On adding all the given reactions (three reactions) the values of K will be multiplied.

4. For the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, K_C at 800° C is 0.1, when equilibrium concentrations of both the reactants are 0.5 molL^{-1}, then value of K_p at above temperature is

(a) 0.5 (b) 0.1 (c) 0.01 (d) 0.05

Hint At equilibrium,

$\because \Delta n = 0, \therefore K_C = K_p = 0.1$

5. $\mathrm{NO}(g) + \frac{1}{2}\mathrm{O}_2(g) \overset{K_1}{\rightleftharpoons} \mathrm{NO}_2(g)$

and $2\mathrm{NO}_2(g) \overset{K_2}{\rightleftharpoons} 2\mathrm{NO}(g) + \mathrm{O}_2(g)$

Then, K_1 and K_2 are related with each other, as

(a) $K_2 = \frac{1}{K_1}$ (b) $K_2 = \frac{K_1}{2}$ (c) $K_2 = \frac{1}{K_1^2}$ (d) $K_2 = \frac{K_1^2}{2}$

Hint Multiply Eq. (i) by 2 and reverse it, K_1 becomes $\frac{1}{(K_1)^2}$

Thus, $K_2 = \frac{1}{K_1^2}$

6. Calculate the partial pressure of CO, if

$$\mathrm{CaCO}_3(s) \xrightarrow{\Delta} \mathrm{CaO}(s) + \mathrm{CO}_2(g); K_p = 8 \times 10^{-2}$$

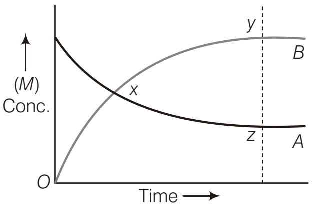
$$\mathrm{CO}_2(g) + \mathrm{C}(s) \longrightarrow 2\mathrm{CO}(g); K_p = 2$$

(a) 0.08 (b) 0.2 (c) 0.4 (d) 4

Hint $K_p(\mathrm{CO}_2) = p(\mathrm{CO}_2) = 8 \times 10^{-2}$ [From Eq. (i)]

$$K_p = \frac{(p(\mathrm{CO}))^2}{p(\mathrm{CO}_2)} \quad \text{[From Eq. (ii)]}$$

7. For the following reaction, $A \rightleftharpoons B$, variation of concentration with time is shown below.



The concentrations A and B are minimum and maximum respectively at points

(a) x and y (b) x and z (c) y and z

(d) any two points between y and z

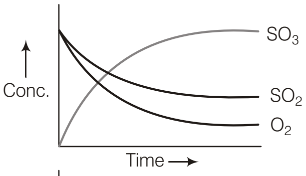
Hint Reversible feature of the reaction starts from point x, thereafter concentration of A starts to decrease and concentration of B starts to increase. At point z concentration of A becomes lowest and constant. At point y-concentration of B becomes maximum and constant.

8. A reaction is carried out in a closed vessel as follows:

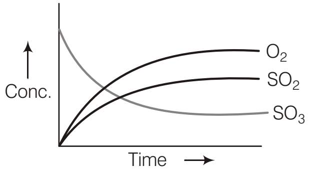
$$2\mathrm{SO}_2(g) + \mathrm{O}_2(g) \rightleftharpoons 2\mathrm{SO}_3(g)$$

If the value of K_{eq} for forward reaction is quite large; which of the following graph is the correct representation for the above reaction?

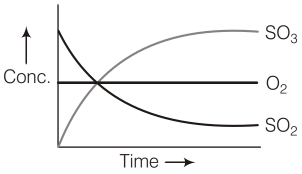
(a)



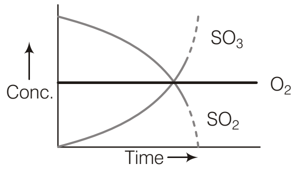
(b)



(c)



(d)



Hint Since, the value of K_{eq} for forward reaction is high. The product SO_3 will be formed to large extent at equilibrium.

9. Sulphide ions in alkaline solution react with solid sulphide to form polysulphide ions having S_2^{2-}, S_3^{2-} etc., ions. If for, $\mathrm{S} + \mathrm{S}^{2-} \rightleftharpoons \mathrm{S}_2^{2-}; K_1 = 12$

$$2\mathrm{S} + \mathrm{S}^{2-} \rightleftharpoons \mathrm{S}_3^{2-}; K_2 = 132$$

The value for K_3, for the following reaction

$$\mathrm{S} + \mathrm{S}_2^{2-} \rightleftharpoons \mathrm{S}_3^{2-}, \text{ will be}$$

(a) 11 (b) 22 (c) 33 (d) 44

10. The rate of reaction for forward reaction is two times that of reverse reaction at given temperature and identical conditions, then K_{eq} will be

(a) 0.5 (b) 1 (c) 1.5 (d) 2

Notice Board

JKCET will be on May 21 & 22, 2016

The Jammu & Kashmir Board of Professional Examination has announced the dates for Jammu & Kashmir Common Entrance Test (JKCET) 2016, conducted for admissions to undergraduate engineering courses across engineering colleges in Jammu & Kashmir. JKCET 2016 is scheduled to be conducted on May 21 and May 22, 2016. Apart from the exam dates, the notification released by the exam conducting authority also published the documents required to be kept ready by a student before filling the Application Form of JKCET 2016. Candidates aspiring for the exam have to be ready with the below mentioned documents for filling the application form:

- Permanent Resident Certificate (State Subject)
- Date of Birth Certificate
- Reserved Category Certificate (if applicable)
- Marks Certificate/Marks Card of qualifying Examination. (If qualifying exam is passed)
- Tuition Fee Waiver Certificates (where Annual income of the parents is less than Rs. 4.50/- Lacs)

LE-CHATELIER'S PRINCIPLE, IONIC EQUILIBRIUM AND OSTWALD'S DILUTION LAW

Le-Chatelier's Principle

When a change is brought about on a system in equilibrium, the system tends to adjust itself to reduce the effect of change.

The Effect of Varying Conditions on the Equilibrium

$$aA + bB \rightleftharpoons cC + dD;\ \Delta n_g = (c + d) - (a + b)$$

Changes imposed on the system in equilibrium	Equilibrium position moves	Equilibrium constant	Any other points
Concentration of *A* and/ or *B* increased	To right	No change	—
Concentration of *C* and/or *D* increased	To left	No change	—
Pressure increased	To right if $(c+d) < (a+b)$, i.e. Δn_g = –ve	No change	Very little effect, if any, on reactions in liquid solution.
	To left if $(c+d) > (a+b)$, i.e. Δn_g = +ve	No change	
	No change if $(c+d) = (a+b)$, i.e $\Delta n_g = 0$	No change	
Temperature increased	To left if ΔH = –ve (exothermic)	Value decreased	Equilibrium achieved faster.
	To right if ΔH = +ve (endothermic)	Value increased	Equilibrium achieved faster.
Addition of a catalyst	No change	No change	Equilibrium achieved faster.

CHEMISTRY CONCENTRATE

TIPS TO SOLVE PROBLEMS RELATED TO LE-CHATELIER'S PRINCIPLE

The following steps can be followed to solve problems related to Le-Chatelier's principle and to decide the favourable conditions for a chemical reaction.

Step 1 Write down the balanced thermochemical equation indicating the phase of each of the reactants and products and the *K* value for the reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta H° = -92\ \text{KJ}$$

$$K_p = \frac{(p^2_{NH_3})}{(p_{N_2}) \times (p^3_{H_2})}$$

Step 2 To increase the concentration of product NH_3, more reactants need to be added or the product need to be removed as soon as it is formed.

Step 3 **Predicting the effect of pressure** Find out Δn_g for the reaction and then apply the fact that when pressure is increased, the reaction shifts in a direction where number of moles decreases.

Here,

$$\Delta n_g = 2 - (3 + 1) = -2$$

Hence, to get more NH_3, pressure needs to be increased.

Step 4 **Predicting the effect of temperature**

For exothermic reaction, decrease in temperature favours forward reaction and for endothermic reaction, increase in temperature favours forward reactions.

Since, the given reaction is exothermic, to get more NH_3, temperature needs to be decreased.

Conclusion Hence, the production of NH_3 can be increased by increasing pressure, decreasing temperature and increasing the concentration of H_2 and N_2.

Ionic Equilibrium

Equilibrium attained between undissociated electrolyte and ions furnished by it in solution is known as ionic equilibrium.

Degree of Dissociation (α)

For a dissociation reaction, degree of dissociation,

$$\alpha = \frac{\text{Total number of moles undergo dissociation}}{\text{Total number of moles taken initially}}$$

$$\begin{array}{llll} & HA & \rightleftharpoons H^+ & + A^- \\ \text{At } t = 0, & n & 0 & 0 \\ \text{At } t, & (n - n\alpha) & n\alpha & n\alpha \end{array}$$

$$\therefore \text{Degree of dissociation} = \frac{n\alpha}{n} = \alpha$$

$$(1 - \alpha \approx 1 \text{ as weak electrolyte})$$

REMEMBER

The value of α depends on

(i) nature of solute.

(ii) nature of solvent (higher the value of dielectric constant of solvent, higher is the value of α).

(iii) Dilution (the value of α of a weak electrolyte increases on dilution).

(iv) Temperature (α increases with increase in temperature).

Ostwald's Dilution Law

For dissociation of a weak electrolyte,

$$\begin{array}{llll} & AB & \rightleftharpoons A^+ & + B^- \\ \text{At}\quad t = 0, & C & 0 & 0 \\ \text{At equilibrium,} & C(1 - \alpha) & C\alpha & C\alpha \end{array}$$

$$\therefore K = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K}{C}} \quad \text{or } \alpha\ \mu\ \frac{1}{\sqrt{C}}\ \mu\ \sqrt{V} \qquad [\because \alpha << 1;\ 1 - \alpha \approx 1]$$

According to this law, "degree of dissociation is proportional to the square root of dilution for weak electrolytes".

Best Practice SHOTS

11. 56 g of N_2 and 8 g of H_2 are heated in a closed vessel. At equilibrium, 34 g of NH_3 is present in the vessel. The number of moles of N_2, H_2 and NH_3 at equilibrium are respectively.

(a) 1, 2, 2 (b) 1, 1, 2 (c) 2, 2, 2 (d) 2, 1, 2

Hint (i) Convert given masses into number of moles.

(ii) At equilibrium, equate number of moles of ammonia equal to 2 and find value of x (dissociated moles of N_2 at equilibrium).

(iii) With the help of x, find the value of number of moles of N_2, H_2 and NH_3 at equilibrium respectively.

12. When alcohol (C_2H_5OH) and acetic acid (CH_3COOH) are mixed together in equimolar proportion, 66.5% of these are converted to ester.

How much ester (in moles) will be formed, if 1 mole of acetic acid and 0.5 mole of alcohol react under same conditions?

(a) 0.423 (b) 1.57 (c) 1.15 (d) 0.545

Hint (i) Calculate the value of K_C with the help of provided percentage of ester.

(ii) Now, calculate number of moles of ester formed from 1 mole of acetic acid.

13. If water and ice are in equilibrium, on applying pressure on the above system.

(a) More ice will form

(b) More ice will melt

(c) Has no effect

(d) Ice becomes gas at same temperature.

Hint Water (ice) $\rightleftharpoons$ Water (liquid)

$\because$ For gases, at equilibrium, value of $\frac{n}{V}$ remains constant, applying pressure, volume of gas decreases.

Since, volume of $W_{(\text{Liquid})} < W_{(\text{Ice})}$

Thus, more ice will melt.

14. Ionisation constant of CH_3COOH is 1.7×10^{-5} and H^+ concentration is 3.4×10^{-4}. Then initial concentration of the acid is

(a) 3.4×10^{-4} (b) 6.8×10^{-3}

(c) 1.7×10^{-3} (d) 3.4×10^{-3}

15. Equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P+Q$, respectively are in the ratio of 1 : 9, if degree of dissociation of X and Z are equal, then the ratio of total pressure at these equilibria is

(a) 1 : 36 (b) 1 : 9

(c) 1 : 1 (d) 1 : 3

Hint For $X \rightleftharpoons 2Y$

Initial 1 0

At equilibrium $1-x$ $2x$

Total number of moles $= 1 - x + 2x = 1 + x$

Thus, $$K_{p_1} = \frac{\left[\frac{2x}{1+x}\right]^2}{\left[\left(\frac{1-x}{1+x}\right)\times p\right]} = \frac{4x^2}{(1-x)}\times\frac{p_1}{(1+x)}$$

Similarly, $$K_{p_2} = \frac{x^2}{(1-x)}\times\frac{p_2}{(1+x)}$$

Therefore, $$\frac{K_{p_1}}{K_{p_2}} = \frac{4\times p_1}{p_2}$$

16. Vapour density of equilibrium mixture of NO_2 and N_2O_4 is found to be 40 for the equilibrium,

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

The degree of dissociation and percentage of NO_2 in the mixture is respectively.

(a) 0.15 and 26% (approx.) (b) 0.15 and 74% (approx.)

(c) 0.85 and 26% (approx.) (d) 0.85 and 74% (approx.)

Hint (i) To find molecular weights calculated and observed.

Let, vapour density (VD) (calculated) = D and VD (observed) = d

(a) Calculated molecular weight = $2\times D$

(b) Observed (exp.) molecular weight = $2\times d$

(ii) To find degree of dissociation

$$\alpha = \frac{D-d}{d}$$

(iii) To find % of NO_2

$N_2O_4 \rightleftharpoons 2NO_2$

Initially 1 0

At equilibrium $1-\alpha$ 2α $\because \alpha = 0.15$

At equilibrium $[NO_2] = 2\times 0.15 = 0.30$

Total number of moles $= 1-\alpha+2\alpha = 1+\alpha = 1.15$

$\therefore$ % of $NO_2 = \frac{2\alpha}{1+\alpha} = \frac{0.30}{1.15}\times 100 = 26.08\%$

17. Consider the following reaction,

$$I_2 + I^- \rightleftharpoons I_3^-$$

This reaction is set up in aqueous medium. We start with 1 mole of I_2 and 0.5 mol of I^- in 1L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mole of yellow precipitate. Calculate the equilibrium constant.

(a) 1.33 (b) 2.66

(c) 2.00 (d) 3.00

Hint Excess $AgNO_3$ gave 0.25 mol of yellow precipitate

$$(AgNO_3 + I^- \longrightarrow \underset{\text{Yellow ppt}}{AgI})$$

$\therefore$ Mole of I_3^- at equilibrium = 0.25

At equilibrium $\underset{1-x}{I_2} + \underset{0.5-x}{I} \rightarrow \underset{x}{I_3}$

Given, $0.5 - x = 0.25$

$x = 0.25$

18. The following reaction occurs in our body.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

If CO_2 escapes from our body,

(a) hydrogen ions concentration will diminish

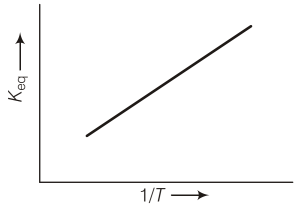
(b) pH will decreases

(c) H_2CO_3 concentration will be altered

(d) forward reaction will be accelerated

Hint When CO_2 escapes, equilibrium shift to the backward direction, thus, H^+ions will diminish.

19. Plot of K_{eq} and inverse of temperature $\left(\frac{1}{T}\right)$ is given; this indicates that reaction must be



(a) exothermic *(b)* endothermic

(c) has no effect of temperature *(d)* All (a), (b) and (c) are wrong

Hint In the given plot,

$$\frac{1}{T} \rightarrow \text{increasing}$$

Means $T \rightarrow$ decreasing

and $T \rightarrow$ decreasing, value of $\ln K_{eq}$ increasing.

Which shows that, the reaction is exothermic by nature.

($\because$ In exothermic reactions, as T decreases value of K increases).

20. For the reaction,

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

The equilibrium is attained at 25°C in a closed vessel and an inert gas (He) is introduced.

Which of the following statement is correct?

(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 changes

(b) More Cl_2 is formed

(c) Concentration of SO_2Cl_2 increased

(d) All above statements are wrong

Hint At constant volume inert gas show no effect at equilibrium.

($\because$ Reactions occur in closed vessel).

pH SCALE, SALT HYDROLYSIS, BUFFER SOLUTIONS AND SOLUBILITY PRODUCT

Ionic Product of Water

Pure water acts as a very weak electrolyte with α equals to 1.8×10^{-9} at 25°C.

For ionisation of water,

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_i = \frac{[H^+][OH^-]}{[H_2O]} \text{ or } K_w = K_i\,[H_2O] = [H^+][OH^-]$$

where, K_w = ionic product of water depends only on temperature.

For pure water, $[H^+] = [OH^-] = 10^{-7}$ M

$$\therefore \quad K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25°C$$

pH Scale

To express the concentration of H^+ ions from 1 M to 10^{-14} M in a simple way, pH scale was introduced in which pH is calculated as

$$pH = -\log[H^+]$$

The $[H^+]$ is always expressed in mol/L.

THE CONCEPT OF NEGATIVE pH

In case of highly concentrated solutions having $[H^+] > 1$ M, the value of $\log[H^+]$ becomes greater than 0, making pH negative. e.g. for 3 M HCl solution, $pH = -\log 3 = -0.4771$ which is negative.

Hence, a negative pH simply means, the $[H^+]$ of the solution is greater than 1M.

A solution having negative pH also occurs naturally in some mine areas, where the minerals form highly concentrated acidic solution.

Similarly, $pOH = -\log[OH^-]$

- pH and pOH are related as
  $pH + pOH = 14 \quad [\because [H^+][OH^-] = 10^{-14}]$
- For neutral solution, $[H^+] = [OH^-]$ or $pH = pOH = 7$

For acidic solution, $[H^+] > [OH^-]$, $pH < 7$

For basic solution, $[H^+] < [OH^-]$, $pH > 7$

CHEMISTRY CONCENTRATE

CALCULATION OF pH IN CASE OF MIXTURE OF ACID AND BASE

The following steps can be followed to find the pH:

***Step* 1** Calculate the moles of the strong acid and strong base present in the solution, e.g. when 100 mL of 1M HCl is mixed with 50 mL of 0.5 M NaOH, Moles of HCl = $M \times V = 100 \times 1 = 100$ m mol

Moles of NaOH = $M \times V = 50 \times 0.5 = 25$ m mol

***Step* 2** Write down the balanced neutralisation reaction occurring in the solution. $HCl + NaOH \longrightarrow NaCl + H_2O$

***Step* 3** Find out the limiting reagent,

	HCl	+ NaOH	$\longrightarrow$ NaCl	+ H_2O
$t = 0$,	100 m mol	25 m mol	0	0
After neutralisation	75 m mol	0	25 m mol	25 m mol

Here, NaOH is the limiting reagent.

***Step* 4** If acid is the limiting reagent, then it will used up completely and the solution will be basic. If base is the limiting reagent, then it will be used up completely and the solution will be acidic. Since, here NaOH is the limiting reagent, the solution will be acidic and pH can be calculated as

$$pH = -\log[H^+],\quad [H^+] = \frac{\text{Moles of } H^+}{\text{Total volume}} = \frac{75 \text{ m mol}}{150 \text{ mL}} = 0.5 \text{ M}$$

$$pH = -\log[H^+] = -\log(0.5) = 0.3$$

Salt Hydrolysis

It is a reverse process of acid-base neutralisation reaction in which the salt reacts with water to form acid and base. Hence, the pH of the resulting solution can be acidic (acidic salt), basic (basic salt) or neutral.

Formulae for pH

Type of acid/base	pH
Strong acid (completely dissociated)	$pH = -\log[H^+]$
Strong base (completely dissociated)	$pOH = -\log[OH^-]$ and $pH = 14 - pOH$
Weak acid (partially dissociated)	$[H^+] = C\alpha = \sqrt{K_aC}$; $pH = \frac{1}{2}(pK_a - \log C)$
Weak base (partially dissociated)	$[OH^-] = C\alpha = \sqrt{K_bC}$; $pOH = \frac{1}{2}(pK_b - \log C)$ $pH = 14 - pOH$
Mixture of weak acids	$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2 \ldots}$; $pH = -\log[H^+]$
Mixture of weak bases	$[OH^-] = \sqrt{K_{b_1}C_1 + K_{b_2}C_2 \ldots}$; $pOH = -\log[OH^-]$
Mixture of strong acid and weak acid	$[H^+] = \frac{C_s + \sqrt{C_s^2 + 4K_aC_w}}{2}$ where, C_s and C_w are concentrations of strong and weak acid respectively.
Mixture of strong acid and strong base	When strong acid and strong base are mixed, neutralisation reaction occur and the final solution may be acidic, basic or neutral based on the equivalents of acid or base left.

In Case of Hydration of Salts

Salt	K_h (Hydrolysis constant)	h (Degree of hydrolysis)	pH of solution
Strong acid + strong base	Hydration do not occur	-	-
Weak acid + Weak base	$\frac{K_w}{K_a \times K_b}$	$\sqrt{\frac{K_w}{K_a \times K_b}}$	$\frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$
Strong acid + Weak base	$\frac{K_w}{K_b}$	$\sqrt{\frac{K_w}{K_b \times C}}$	$\frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$
Weak acid + strong base	$\frac{K_w}{K_a}$	$\sqrt{\frac{K_w}{K_a \times C}}$	$\frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$

Buffer Solution

A solution, which maintains its pH constant even upon addition of small amount of acid or base.

- Mixed buffers are the solutions of more than one compound. These are classified into following types:
  - (i) Acidic buffer (ii) Basic buffer
  - (iii) A mixture of polyprotic acid and its acidic salt.
  - (iv) Buffer containing amphoteric electrolyte such as amino acids.

	Acidic buffer	Basic buffer
1.	It is a mixture of weak acid and its salt with strong base, e.g. $CH_3COOH + CH_3COONa$	It is a mixture of weak base and its salt with a strong acid, e.g. NH_4OH and NH_4Cl.
2.	Its pH can be calculated as $pH = pK_a + \log\frac{[Salt]}{[Acid]}$	Its pOH can be calculated as $pOH = pK_b + \log\frac{[Salt]}{[Base]}$

Importance of pH

For humans	For animals	For soils and plant growth
▪ For good digestion pH in stomach and small intestine should be approximately 1.5 and 8.4 respectively. ▪ The blood that goes to the heart and lungs, should have pH ~ 6.5 means it should be slightly acidic. ▪ Our mouth pH should not be lower than 5.5 otherwise tooth decay can start. ▪ Bacteria present in our mouth produce acids by degradation of sugar and food particles. ▪ The best way to prevent from this is to clean the mouth after eating.	▪ The aquatic animals (like fish) can survive in river water within a narrow pH range. ▪ When the pH of rain water in about 5.6, it is called acid rain. Too much acid rain can lower the pH of river water to such an extent that the survival of aquatic animals become difficult ▪ The high acidity of river water even kill the aquatic animals.	▪ Most of the plants grow best when the pH of the soil is close to 7. ▪ If the soil is too acidic or too basic, the plants grow badly or do not grow at all. ▪ The soil pH is also affected by the use of chemical fertilisers in the field. ▪ If soil is too acidic, it is treated with materials like, quick lime or slaked lime or chalk. ▪ If soil is alkaline, it is treated with organic matter which is acidic.

Solubility and Solubility Product

Salts can be either completely soluble (NaCl, Na_2SO_4 etc), sparingly soluble ($Mg(OH)_2$, AgCl etc) or insoluble (LiF) in a given amount of solvent.

- In case of sparingly soluble salt, the salt dissolves till a saturated solution is obtained. After saturation, if we further add the salt, then precipitation occurs.
- For a sparingly soluble salt, if S is the molar solubility,

$$A_xB_y(s) + H_2O \rightleftharpoons xA^{y+} + yB^{x-}(aq)$$

At saturation, $K[A_xB_y(s)] = [A^{y+}]^x \times [B^{x-}]^y = [xS]^x[yS]^y$

$$\text{or} \quad K_{sp} = x^x \times y^y S^{x+y} \quad \text{or} \quad S = \left(\frac{K_{sp}}{x^x y^y}\right)^{1/x+y}$$

Conditions for Precipitation

(i) When ionic product, $[A^{y+}]^x[B^{x-}]^y < K_{sp}$, the solution is unsaturated and no precipitation occurs.

(ii) When ionic product $= K_{sp}$, the solution becomes just saturated.

(iii) When ionic product $> K_{sp}$, the solution becomes saturated enough and precipitation occurs to make ionisation product equals to K_{sp}.

Common Ion Effect

The phenomenon in which the degree of dissociation of a weak electrolyte is suppressed by adding a substance having an ion common to the weak electrolyte, e.g. the dissociation of CH_3COOH can be suppressed by adding CH_3COONa.

Applications of Common Ion Effect and Solubility Product

- Pure NaCl is recovered from sea water by passing dry HCl gas over crude salt (contains impurities like $CaCl_2$, KBr etc). The ionic product of NaCl exceeds its solubility product due to the addition of HCl and it is precipitated as pure NaCl. It is further purified by crystallisation.
- Precipitation of salts during qualitative inorganic analysis is also based on the principle of solubility product and common ion effect.

Best Practice SHOTS

21. The pH of 0.1 M CH_3COOH which is 2% ionised in aqueous solution is

(a) 2.0 *(b)* 1.0 *(c)* 2.7 *(d)* 11.3

22. For the reaction,

$$NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

If equilibrium pressure is 3 atm, then value of K_{sp} is

(a) 4 *(b)* 27 *(c)* 1/4 *(d)* 1/27

23. pH of a reaction between 0.1 N NH_4OH and 0.1 N HCl will be

(a) equal to 7 *(b)* more than 7

(c) less than 7 *(d)* equal to 14

24. Fear or excitement, causes one to breathe rapidly which results a decrease in CO_2 concentration in blood. In what way will it change the pH of blood?

(a) pH will increase *(b)* pH will decrease

(c) No effect on pH *(d)* pH becomes zero

Hint Blood is buffer solution of H_2CO_3 / HCO_3^- thus, pH remains same.

25. Which of the following salts undergoes for anionic hydrolysis?

(a) NH_4Cl *(b)* $FeCl_3$ *(c)* Na_2CO_3 *(d)* $CuSO_4$

Hint Anionic hydrolysis means anionic part of the salt will react with water, while cationic part comes from strong base remain as such in the solution.

$$Na_2CO_3 + 2H_2O \longrightarrow 2Na^+ + 2OH^- + H_2CO_3$$

Note (i) Ions of strong acid or base are weak ions, they do not react with water.

(ii) Ions of weak acid or base are strong ions and will react with water.

(i.e. combine with counter part, i.e. acidic radicals with H^+ ions and basic radicals with OH^- ions).

The process is called hydrolysis.

26. What is the pH of 10^{-3} M, OH^- ion solution at 333 K, if K_w at 333 K is $10^{-12.6}$?

(a) 4 *(b)* 9 *(c)* 9.02 *(d)* 9.6

Hint At 333 K, $pK_w = 12.6$

27. Solubility products (K_{sp}) of salts of type MX, MX_2 and M_2X_3 at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15} respectively.

Solubilities (in mol L^{-1}) of these salts at temperature (T) are in order.

(a) $MX > M_2X_3 > MX_3$ *(b)* $M_2X_3 > MX_2 > MX$

(c) $MX > M_2X_3 > MX_2$ *(d)* $MX_2 > M_2X_3 > MX$

28. On adding 0.1 M solution of each Ag^+, Ba^{2+} and Ca^{2+} ions in Na_2SO_4 solution. Species first precipitate is (Given, K_{sp} for $CaSO_4 = 10^{-6}$, $BaSO_4 = 10^{-11}$ and $Ag_2SO_4 = 10^{-5}$)

(a) Ag_2SO_4 *(b)* $CaSO_4$ *(c)* $BaSO_4$

(d) All precipitate at the same time

Hint

(i) For similar type (i.e. AB type e.g. $CaSO_4$ and $BaSO_4$) of salts more be the value of K_{sp}, more be the solubility of that salt.

(ii) Between AB and A_2B type.

(e.g. $CaSO_4$ and Ag_2SO_4)

S for AB type $= \sqrt{K_{sp}}$; ($\because K_{sp} = S^2$)

and S for A_2B type $= \left(\frac{K_{sp}}{4}\right)^{1/3}$; ($\because K_{sp} = 4S^3$)

Obviously, the value of 'S' in case of AB is larger as compared to A_2B type, unless the value of K_{sp} for A_2B type is very large, (e.g. as in case of $BaSO_4$ and Ag_2SO_4)

29. A solution has pH = 5 is diluted to 100 times. The new solution becomes

(a) acidic *(b)* basic

(c) no change *(d)* neutral

Hint After dilution $[H^+] = \frac{10^{-5}}{100} = 10^{-7}$

30. Which has highest pH in solution?

(a) CH_3COOH *(b)* Na_2CO_3

(c) NH_4Cl *(d)* $NaNO_3$

Hint $\because$ Na_2CO_3 solution is basic by nature, solution of CH_3COOH and NH_4Cl is acidic by nature, while $NaNO_3$ solution is neutral.

Thus, pH of Na_2CO_3 is highest.

31. pK_a of HCN is 9.30, the pH of solution, prepared by mixing 2.5 mol of KCN and 2.5 mol of HCN in water, so that total volume becomes 500 mL is

(a) 9.3 *(b)* 0.93 *(c)* 3.9 *(d)* 0.39

32. pH of a weak acid (HA) is 3 if concentration of weak acid is 0.1 M, then its degree of dissociation is

(a) 1% *(b)* 10% *(c)* 50% *(d)* 99%

33. A certain buffer solution contains equal concentration of X^- ions and HX. The K_a for HX is 10^{-8}, the pH of this buffer solution is

(a) 3 *(b)* 8 *(c)* 11 *(d)* 6

34. Precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) will be obtained, when equal volume of the followings is mixed.

(a) 10^{-4} M, Ca^{2+} ions and 10^{-4} M, F ions

(b) 10^{-2} M, Ca^{2+} ions and 10^{-8} M, F ions

(c) 10^{-2} M, Ca^{2+} ions and 10^{-3} M, F ions

(d) 10^{-3} M, Ca^{2+} ions and 10^{-5} M, F ions

Hint For precipitation, ionic product should be greater than solubility product.

35. The compound whose 0.1 M solution is basic is

(a) ammonium acetate

(b) ammonium chloride

(c) ammonium sulphate

(d) sodium acetate

Answers

1. (a)	**2.** (a)	**3.** (c)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (a)	**9.** (a)	**10.** (d)
11. (b)	**12.** (a)	**13.** (b)	**14.** (b)	**15.** (a)	**16.** (a)	**17.** (a)	**18.** (a)	**19.** (a)	**20.** (d)
21. (c)	**22.** (a)	**23.** (c)	**24.** (c)	**25.** (c)	**26.** (d)	**27.** (c)	**28.** (c)	**29.** (d)	**30.** (b)
31. (a)	**32.** (a)	**33.** (b)	**34.** (c)	**35.** (d)					

MASTER STROKE

1. Which causes largest change in pH on adding 20 mL, 0.1 M acetic acid solution to

(a) distilled water
(b) 20 mL of 0.01 M CH_3COOH
(c) 20 mL of 0.01 M NaOH
(d) 20 mL of 0.01 M HCl

Hint pH changes when solution becomes neutral or basic from acidic.

2. At equilibrium, a 500 mL vessel contains 1.5 M of each $A + B \rightleftharpoons C + D$, if 0.5 M of C and D expelled out, at equilibrium, what would be the value of K_C.

(a) 1 *(b)* $\frac{1}{9}$
(c) $\frac{1}{4}$ *(d)* $\frac{4}{9}$

Hint $A + B \rightleftharpoons C + D$

At equilibrium = 1.5 1.5 1.5 1.5 (Given)

$$K_C = \frac{\text{Concentration of products}}{\text{Concentration of reactants}}$$

Value of K_C does not depend on concentration.

Initial concentration at equilibrium is 1, (∵ all are at same concentration and have same number of moles at equilibrium). Thus, value of K_C remains as before the reaction after removal of 0.5 mole of C and D, reaction readjust itself to attain the same value of K_C.

3. When two reactants A and B are mixed to give products C and D, at equilibrium the value of reaction quotient (Q)

(a) decreases with time
(b) increases with time
(c) becomes zero at equilibrium
(d) is independent with time

Hint Q is zero at $t = 0$ and increases with time.

At equilibrium $Q = K_{eq}$

4. The pK_a of HCN is 9.30, the pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up the total volume to 500 mL is

(a) 7.30 *(b)* 8.30
(c) 9.30 *(d)* 10.30

5. 0.365 g of HCl gas was passed through 100 cm^3 of 0.2 M NaOH solution. The pH of the resulting solution would be

(a) 1 *(b)* 5
(c) 9 *(d)* 13

Hint (i) Calculate the number of moles of HCl and NaOH.

(ii) At neutralisation point find out which species (acid or base) remains in the solution and calculate pH of the solution.

6. A solution which is 10^{-3} M of each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ions. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, Which one will precipitate first?

(a) FeS *(b)* HgS
(c) ZnS *(d)* MnS

7. What is the pH of 10^{-3} M ammonium cyanide solution, if $K_{HCN} = 7.2 \times 10^{-11}$ and $K_{NH_3} = 1.8 \times 10^{-5}$ mol L^{-1}?

(a) 7.5 *(b)* 9.7
(c) 12 *(d)* 14

8. For a given reaction,
$2X(g) + Y(g) \rightleftharpoons Z(g) + 75$ kcal; which combination of pressure and temperature give highest yield of Z at equilibrium?

(a) 1000 atm and 100°C
(b) 1000 atm and 500°C
(c) 100 atm and 500°C
(d) 10 atm and 500°C

Hint (i) For the given reaction $\Delta n_g = -ve$.

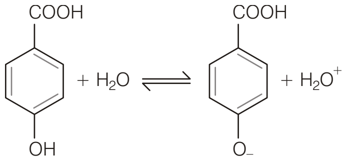
Thus, high pressure favours formation of product.

(ii) For the given reaction, value of $\Delta H = -ve$.

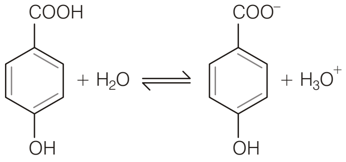
Thus, low temperature is favourable.

9. Which H^+ is removed in step I?

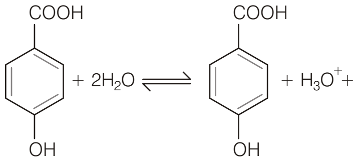
(a)



(b)



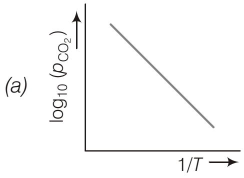
(c)

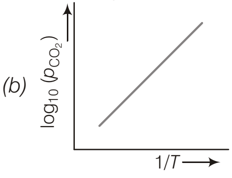


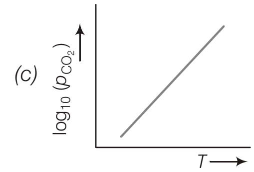
(d) 50% H^+ ions comes from (a) and 50% H ions comes from (b)

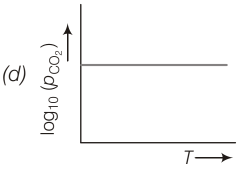
Hint ∵ K_a for ¾ COOH group > K_a for ¾ OH group, also ¾ COOH is more reactive and acidic as compared to ¾ OH group.

10. For a reaction at equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the value of ΔH_R° can be represented, by which of the following curve?

(a)


(b)


(c)


(d)


Hint $\because \log_{10} K_p = \log_{10} A - \dfrac{\Delta H_R^\circ}{2.303\,RT}$ on comparing with equation of straight line equation.

$$y = mx + c,\ y = \log K_p = \log_{10} p_{(CO_2)}$$
$$x = \frac{1}{T},\qquad m = -\Delta H_R^\circ/2.303\,R$$

Thus, slope as shown in curve (a) is the right choice.

11. For a reversible equilibrium reaction, $A + B \rightleftharpoons AB$,
The true statement is

- (a) Both reactions are endothermic
- (b) Both reactions are exothermic
- (c) Association reaction is endothermic and dissociation reaction is exothermic
- (d) Association reaction is exothermic and dissociation reaction is endothermic

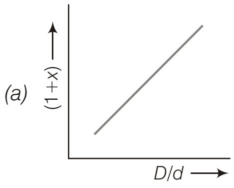
Hint In association, bond is formed between A and B, thus release energy, hence is an exothermic process while, during dissociation, energy is required to break the bonds ($A - B$). Thus, is an endothermic process.

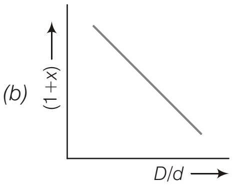
12. pH of 10^{-8} M, NaOH solution will be
(Given, $\log 11 = 1.04$)

(a) 6.96 (b) 7.04 (c) 8 (d) 12

Hint Total $[OH^-] = 10^{-8}$ M from NaOH + 10^{-7} M from H_2O
$= 11 \times 10^{-8}$ M

13. In dissociation of N_2O_4 into NO_2, $(1 + x)$ varies with the vapour densities ratio $\dfrac{D}{d}$ as

(a)


(b)


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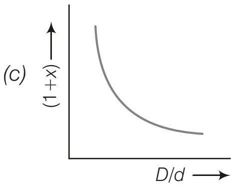

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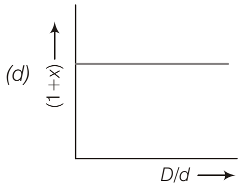
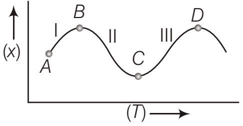


Hint $(1 + x)$ is total number of moles which remains constant throughout the reaction.

14. For the reaction, passes through the following three stages I, II and III, $A \xrightarrow{\text{I}} B \xrightarrow{\text{II}} C \xrightarrow{\text{III}} D$ quantity of product formed (x), varies with temperature (T) will be



- (a) Stages I and III are exothermic and II is endothermic
- (b) Stages I and III are endothermic and II is exothermic
- (c) Stages II and III are exothermic and I is endothermic
- (d) Stages I and II are endothermic and III is exothermic

Hint For Stage I-x increases as T increases.

Thus, is endothermic.

For Stage II-x decreases as T increases

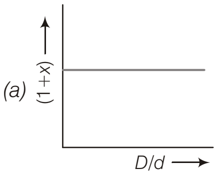
Thus, is exothermic.

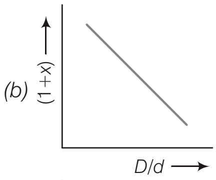
For Stage III-x increases as T increases.

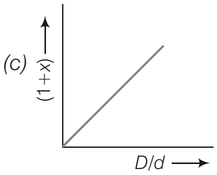
Thus, is endothermic.

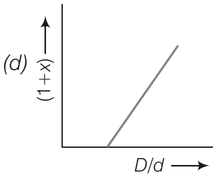
Hence, I and III are endothermic and II is exothermic.

15. For dissociation of PCl_5 into PCl_3 and Cl_2 in gaseous phase reaction. If d is the observed vapour pressure (exp.) and D is the theoretical (calculated) vapour density with 'x' as degree of dissociation, variation of $\dfrac{D}{d}$ with x is given by

(a)


(b)


(c)


(d)


Answers

1. (c)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (b)	**8.** (a)	**9.** (b)	**10.** (a)
11. (d)	**12.** (b)	**13.** (d)	**14.** (b)	**15.** (d)					

Redox Reactions

INTRODUCTION, OXIDATION NUMBER, TYPES OF REDOX REACTIONS

In a redox reaction, both oxidation and reduction occur simultaneously.

Redox reaction

Oxidation	Reduction
Addition of oxygen/ electronegative element (or) removal of hydrogen/electropositive element (or) loss of electron(s).	Removal of oxygen/ electronegative element (or) addition of hydrogen/electropositive element (or) gain of electron(s).

An oxidising agent (oxidant) helps in oxidation of other species by accepting electrons lost during oxidation and itself gets reduced. A reducing agent (reductant) helps in reduction by donating electrons to the species undergoing reduction and itself gets oxidised.

REMEMBER

- Elements in their highest oxidation state in a compound always act as oxidising agent as they always get reduced. e.g. $K\underline{Mn}O_4$, $K_2\underline{Cr}_2O_7$, $H_2\underline{S}O_4$, $H\underline{Cl}O_4$, $H\underline{N}O_3$, $\underline{S}O_3$, $\underline{Cr}O_3$, $\underline{C}O_2$, etc.
- Elements in their lowest oxidation state in a compound always act as reducing agent as they always get oxidised. e.g. H_2S, most of the metals, etc.
- Elements having intermediate oxidation state can act as oxidising as well as reducing agents, e.g. $\underline{S}O_2$, $\underline{Fe}^{2+}$, $\underline{Mn}O_2$, $\underline{I}O^-$, etc.

Oxidation Number (ON)

- Oxidation number of an element in a particular compound is equal to the number of electrons lost, gained or shared by that compound. It is positive when electrons are lost and negative when electrons are gained.

Rules for Finding Oxidation Number

1. Oxidation number of an atom in free state is always 0. e.g. oxidation number of H in H_2, O in O_2, Cl in Cl_2, Na, K, Fe etc., is zero.
2. Oxidation number of hydrogen in a compound is always +1 except in case of metal hydrides (NaH, CaH_2, etc) where the oxidation number of H is –1.
3. Oxidation number of oxygen in a compound is always -2 except in peroxides (H_2O_2, Na_2O_2, etc) where it is -1, in superoxides (KO_2, etc) it is $-1/2$ and in OF_2, it is $+2$.
4. Oxidation number of fluorine in a compound is always -1.
5. Oxidation number of alkali metals and alkaline earth metals in a compound are always $+1$ and $+2$ respectively.
6. Oxidation number of metals are always positive, except in some metallic hydrides like $CuH\,(-1)$ and metal carbonyls such as $[Rh(CO)_4]^-$.
7. The algebraic sum of oxidation number of all atoms in a neutral compound is always zero and in an ion, it is equal to the total charge on the ion.

Types of redox reactions

Intermolecular redox reaction	Intramolecular redox reaction	Disproportionation reaction
Two different molecules/compounds are oxidised and reduced. e.g. $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$	Different elements of same compound is oxidised as well as reduced. e.g. $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$	(Auto-redox) A single atom in a molecule compound is oxidised as well as reduced. e.g. $I_2 \rightarrow I^- + IO_3^-$

Best Practice SHOTS

1. Arrange the followings in the increasing oxidation number of Mn, N and X respectively.

(a) $MnCl_2$, MnO_2, $KMnO_4$

(b) N_2O, NH_3, N_3H, NO, N_2O_5

(c) HXO, HXO_3, HXO_2, HXO_4

Hint (a) $MnCl_2 < MnO_2 < KMnO_4$

(b) $NH_3 < N_3H < N_2O < NO < N_2O_5$

(c) $HXO < HXO_2 < HXO_3 < HXO_4$

2. Find out the oxidation number of Cr in CrO_2Cl_2, $Na_2Cr_3O_{10}$ and $Cr_2(SO_4)_3$ respectively.

Hint +6, +6 and +3

3. Find out the oxidation number of elements underlined in each case.

(a) $\underline{Fe}SO_4(NH_4)_2SO_4 \cdot 6H_2O$.

(b) $Na_2\underline{S}_4O_6$

(c) $Na_2[\underline{Fe}(CN)_5NO]$

Hint (a) $x - 2 + 0 + 0 = 0,\ x = 2$

(b) $2 \times (1) + 4x + 6 \times (-2) = 0,\ x = 5/2$

(c) $2 + x + 5(-1) + 1 = 0,\ x = 2$

4. Write down the name of the following redox reactions.

(a) $H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

(b) $Fe + N_2H_4 \longrightarrow NH_3 + Fe(OH)_2$

(c) $2KClO_3 \longrightarrow 2KCl + 3O_2$

Hint (a) Disproportionation reaction

(b) Intermolecular redox reaction

(c) Intramolecular redox reaction

5. Find out the oxidation number of sulphur in the following compounds: HSO_3^-, $S_2O_8^{2-}$, $S_2O_4^{2-}$, H_2S and H_2SO_4.

Hint The oxidation number of sulphur in HSO_3^-, $S_2O_8^{2-}$, $S_2O_4^{2-}$, and H_2SO_4 are +4, +7, +3, −2 and +6 respectively.

6. What is the highest oxidation number of P, S and I?

Hint Highest oxidation number of $P = +5, S = +6, I = +7$

7. Write the following equations in ionic form,

(a) $NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$

(b) $K_2Cr_2O_7 + 14HI \longrightarrow 2CrI_3 + 2KI + 3I_2 + 7H_2O$

Hint (a) $Na^+ + HCO_3^- + 2H^+ + SO_4^{2-} \longrightarrow$

$2Na^+ + SO_4^{2-} + H_2O + CO_2$

or $Na^+ + HCO_3^- + 2H^+ \longrightarrow 2Na^+ + H_2O + CO_2$

(b) $2K^+ + Cr_2O_7^{2-} + 14H^+ + 14I^- \longrightarrow$

$2Cr^{3+} + 6I^- + 2K^+ + 2I^- + 3I_2 + 7H_2O$

or $14H^+ + Cr_2O_7^{2-} + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

8. Which of the reactant act as oxidant and reductant in the following reaction?

(a) $KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$

(b) $C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$

Hint (a) Oxidant $\Rightarrow KIO_3$, Reductant $\Rightarrow KI$

(b) Oxidant $\Rightarrow Br_2$, Reductant $\Rightarrow C_2H_4$

9. Sulphur dioxide (SO_2) under atmospheric condition changes into SO_x^{2-}. If the oxidation number of S in SO_x^{2-} is +6. What is the value of x in SO_x^{2-}?

Hint The value of $x = 4$

$\Rightarrow \quad +6 - 2x = -2 \Rightarrow +6 + 2 = 2x; \quad 8 = 2x; \quad x = 4$

10. Name one compound each in which oxidation number of

(a) oxygen is +2 (b) nitrogen is +1 (c) chlorine is +4

Hint (a) F_2O (b) N_2O (c) ClO_2

11. Why $HgCl_2$ and $SnCl_2$ cannot exist as such if present together in an aqueous solution?

Hint When both $HgCl_2$ and $SnCl_2$ present together, undergoes redox reaction (double displacement occur) and a white precipitate will formed.

$$2HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + \underset{\text{(white ppt)}}{Hg_2Cl_2} \downarrow$$

BALANCING OF REDOX REACTIONS

Balancing of Redox Reaction

While balancing a redox reaction, both mass and charge must be balanced on both sides of the chemical reaction. The following are different methods followed while balancing a redox reaction.

(a) Half-cell Reaction Method

This method is usually followed while balancing redox reaction occurs inside a cell.

Steps followed while balancing a redox reaction using half-cell reaction method

Step 1 Assign oxidation state to the elements undergoing oxidation and reduction,

e.g. $\overset{0}{I_2} + \overset{+2}{S_2}O_3^{2-} \longrightarrow \overset{-1}{I^-} + \overset{2.5}{S_4}O_6^{2-}$

Here, I_2 is reduced and $S_2O_3^{2-}$ is oxidised.

Step 2 Write down the oxidation half-cell and reduction half-cell separately.

$I_2 \longrightarrow I^-$ (Reduction half-cell)

$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$ (Oxidation half-cell)

Step 3 Balance charge and mass of each half-cell separately.

$I_2 + 2e^- \longrightarrow 2I^-; \quad 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

Step 4 Equalise the number of electrons on opposite side of the oxidation and reduction half-cell by multiplying with suitable coefficients so that these would cancel out while adding.

Since, there are same number of electrons on both sides, hence there is no need to multiply by coefficients.

Step 5 Add both the oxidation and reduction half-cell equations to get the final balanced equation.

$$\begin{array}{l} I_2 + 2e^- \longrightarrow 2I^- \\ 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \\ \hline I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \end{array}$$

(Final balanced redox reaction)

(b) Oxidation Number Change Method

This method is also similar to half-cell reaction method but here the two half-cell reactions are not separated.

REMEMBER

We can balance redox reactions occurring in acidic and basic medium by following both of the above methods. Here, we follow one more step to balance H and O-atoms in both acidic and basic medium as discussed on the next page.

Steps followed to balance redox reactions in acidic medium by oxidation number change method

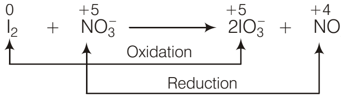
Step 1 Assign oxidation number of elements undergoing oxidation and reduction.

$$\overset{0}{I_2} + \overset{+5}{N}O_3^- \longrightarrow \overset{+5}{I}O_3^- + \overset{+4}{N}O_2$$

Step 2 Balance only those elements that undergo a change in oxidation state. Here, I and N-atom undergo a change in oxidation state.

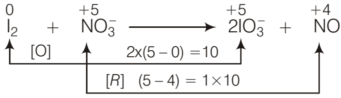
$$I_2 + NO_3^- \longrightarrow 2IO_3^- + NO_2$$

Step 3 Connect the elements undergoing oxidation and reduction by a closed bracket. Here, I_2 undergoes oxidation and N-atom of NO_3^- undergoes reduction.



Step 4 Indicate the increase in oxidation number for oxidation reaction and decrease in oxidation number for reduction reaction. Multiply them with suitable coefficients to make the increase in oxidation number in oxidation process equal to the decrease in oxidation number in reduction process.

Here, we need to multiply the reduction reaction by 10.



Step 5 Write down the new equation after multiplying by coefficients and balance all elements except H and O.

$$I_2 + 10NO_3^- \longrightarrow 2IO_3^- + 10NO_2$$

Here, all elements except O-atom are balanced.

Step 6 In acidic medium, for each excess O-atom, add one H_2O molecule on opposite side and $2H^+$ on same side. There are 4 extra O-atom on reactants side. Hence,

$$I_2 + 10NO_3^- + 8H^+ \longrightarrow 2IO_3^- + 10NO_2 + 4H_2O$$

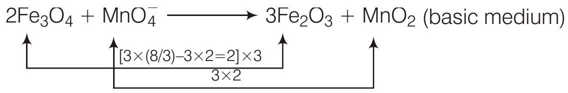
Now, the reaction is balanced.

Steps followed to balance redox reaction in basic medium by oxidation number change method

The first five steps followed while balancing a redox reaction in acidic medium is also followed here. However, while balancing H and O, we follow a different method as described below

Step 6 In basic medium, for each excess O-atom, add one H_2O on same side and $2OH^-$ (basic) on opposite side.

If H-atoms are not yet balanced, for one excess H add one OH^- on same side and one H_2O on the opposite side, e.g.



$$6Fe_3O_4 + 2MnO_4^- \longrightarrow 9Fe_2O_3 + 2MnO_2 \text{ (Basic medium)}$$

$$\text{(1 excess O-atom) } H_2O \longrightarrow 2\overset{-}{O}H$$

$$6Fe_3O_4 + 2MnO_4^- + H_2O \longrightarrow 9Fe_2O_3 + 2MnO_2 + 2OH^-$$

(Final balanced equation)

Applications of Redox Reactions

- Redox reactions are used in a wide range of industrial applications, e.g. in metallurgical processes for extracting metals from their ores, combustion of fuels and energy generating using electrochemical cells.
- In photosynthesis process, green plants convert carbon dioxide and water into carbohydrates in presence of sunlight. During this reaction, CO_2 is reduced to carbohydrates while water is oxidised to oxygen. The energy need for the reaction is provided by sunlight and sensitised by chlorophyll.
- Many chemicals of our daily needs such as chlorine, caustic soda, etc., are produced by electrolysis which is based on redox reactions.
- In quantitative analysis, redox titrations involve the reactions between oxidising and reducing agents and help in estimating the amount of unknown substances in solutions.

Best Practice SHOTS

12. Balance the following equations,

(a) $BaCrO_4 + KI + HCl \longrightarrow BaCl_2 + I_2 + KCl + CrCl_3 + H_2O$

(b) $Mn_2O_7 \longrightarrow MnO_2 + O_2$

(c) $As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$

Hint (a) $2BaCrO_4 + 6KI + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 6KCl + 2BaCl_2 + 8H_2O$

(b) $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

(c) $3As_2S_3 + 28HNO_3 + 4H_2O \longrightarrow 6H_3As_3O_4 + 9H_2SO_4 + 28NO$

13. Balance the following equations in acidic medium.

(a) $HCl + KMnO_4 \longrightarrow Cl_2 + KCl + MnCl_2$

(b) $HNO_3 + HBr \longrightarrow NO + Br_2 + H_2O$

(c) $Cu^{2+} + SO_2 \longrightarrow Cu^+ + SO_4^{2-}$

Hint (a) $16HCl + 2KMnO_4 \longrightarrow 5Cl_2 + 2KCl + 2MnCl_2 + 8H_2O$

(b) $2HNO_3 + 6HBr \longrightarrow 2NO + 3Br_2 + 4H_2O$

(c) $2Cu^{2+} + SO_2 + 2H_2O \longrightarrow 2Cu^+ + 4H^+ + SO_4^{2-}$

14. Balance the following equations in basic medium.

(a) $MnO_4^- + Fe^{2+} \xrightarrow{\overset{-}{O}H} Mn^{2+} + Fe^{3+}$

(b) $S_2O_4^{2-} + Ag_2O \xrightarrow{\overset{-}{O}H} Ag + SO_3^{2-}$

(c) $H_2 + ReO_4^- \xrightarrow{\overset{-}{O}H} ReO_2 + H_2O$

(d) $ClO_2 + SbO_2^- \xrightarrow{\overset{-}{O}H} ClO_2^- + Sb(OH)_6^-$

Hint (a) $MnO_4^- + 5Fe^{2+} + 4H_2O \longrightarrow Mn^{2+} + 5Fe^{3+} + 8\bar{O}H$

(b) $S_2O_4^{2-} + Ag_2O + 2\bar{O}H \longrightarrow 2Ag + 2SO_3^{2-} + H_2O$

(c) $3H_2 + 2ReO_4^- \longrightarrow 2ReO_2 + 2H_2O + 2\bar{O}H$

(d) $2ClO_2 + SbO_2^- + 2\bar{O}H + 2H_2O \longrightarrow 2ClO_2^- + Sb(OH)_6^-$

15. Balance the following equations by ion electron (half-reaction) method for each of the following equations.

(a) $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$
(b) $H_2O_2 + I^- + H^+ \longrightarrow H_2O + I_2$
(c) $Cr_2O_7^{2-} + C_2H_4O + H^+ \longrightarrow Cr^{3+} + C_2H_4O_2 + H_2O$
(d) $Cu_2O + H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + H_2O$

Hint (a) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(b) $H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$

(c) $Cr_2O_7^{2-} + 8H^+ + 3C_2H_4O \longrightarrow 2Cr^{3+} + 4H_2O + 3C_2H_4O_2$

(d) $3Cu_2O + 14H^+ + 2NO_3^- \longrightarrow 6Cu^{2+} + 7H_2O + 2NO$

16. Balance the following equations by oxidation number method :

(a) $Cl_2 + IO_3^- \longrightarrow Cl^- + IO_4^-$ (in basic medium)
(b) $MnO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + MnO_2$
(c) $Fe^{3+} + Sn^{2+} \longrightarrow Sn^{4+} + Fe^{2+}$
(d) $Zn + NO_3^- \longrightarrow Zn^{2+} + NH_4^+$

Hint (a) $Cl_2 + IO_3^- + 2\bar{O}H \longrightarrow 2Cl^- + IO_4^- + H_2O$

(b) $2H^+ + 2Mn\bar{O}_4 + 3SO_3^{2-} \longrightarrow 2MnO_2 + 3SO_4^{2-} + H_2O$

(c) $2Fe^{3+} + Sn^{2+} \longrightarrow Sn^{4+} + 2Fe^{2+}$

(d) $4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

17. Use the arbitrary coefficient method to balance the following equations.

(a) $Pb(N_3)_2 + Co(MnO_4)_3 \longrightarrow CoO + MnO_2 + Pb_3O_4 + NO$
(b) $K_4[Fe(CN)_6] + KOH + Ce(NO_3)_4 \longrightarrow Fe(OH)_3 + Ce(OH)_3 + K_2CO_3 + KNO_3 + H_2O$

Hint (a) $30Pb(N_3)_2 + 44Co(MnO_4)_3 \longrightarrow 44CoO + 132MnO_2 + 10Pb_3O_4 + 180NO$

(b) $K_4[Fe(CN)_6] + 258KOH + 61Ce(NO_3)_4 \longrightarrow Fe(OH)_3 + 61Ce(OH)_3 + 250KNO_3 + 6K_2CO_3 + 36H_2O$

MASTER STROKE

1. Why H_2O_2 acts as a reductant as well as an oxidant?

Hint Oxidation number of O in H_2O_2 is –1. Maximum oxidation state of O is +2 and minimum is –2.

Explanation Hydrogen peroxide has the ability to gain or lose electrons, as its oxygen atoms are in the +1 oxidation state. By gaining electrons they can go to –2 oxidation state and by losing electrons they can go to the zero oxidation state.

2. Which of the followings is/are oxidant and which is/are reductant?

Br_2, Fe^{3+}, I^-?

Hint $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ [oxidant]
$Br_2 + 2e^- \longrightarrow 2Br^-$ [oxidant]
$2I^- \longrightarrow I_2 + 2e^-$ [reductant]

3. Find out the oxidation numbers of Cl in Cl_2, HOCl, Cl_2O, ClO_2, $KClO_3$ and Cl_2O_7.

Hint The oxidation number of Cl in Cl_2, HOCl, Cl_2O, ClO_2, $KClO_3$ and Cl_2O_7 are 0, +1, +1, +4, +5 and +7 respectively.

4. Find out the oxidation number of underlined atom.

$[\underline{Co}(NH_3)_6]^{3+}$, $K\underline{Cr}O_3Cl$, $\underline{P}_2O_7^{4-}$, $\underline{Cl}O_2^-$

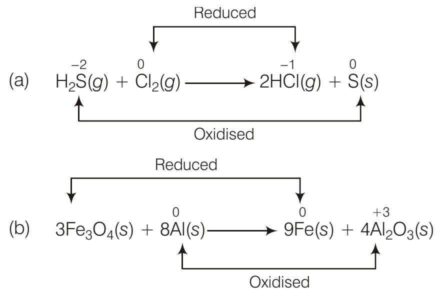
Hint $\underline{Co}(NH_3)_6^{3+} = +3$, $K\underline{Cr}O_3Cl = +6$; $\underline{P}_2O_7^{4-} = +5$; $\underline{Cl}O_2^- = +3$

5. Identify the species undergoing oxidation and reduction.

(a) $H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S(s)$

(b) $2Fe_3O_4(s) + 8Al(s) \longrightarrow 9Fe(s) + 4Al_2O_3(s)$

Hint



In Fe_3O_4, Fe exists in both +2 and +3 oxidation states.

6. Write one equation each for decomposition reactions where energy is supplied in the form of heat, light or electricity.

Hint Heat $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

Light $2AgCl(s) \xrightarrow{h\nu} 2Ag(s) + Cl_2(g)$

Electricity $2H_2O(l) \xrightarrow{\text{Electric current}} 2H_2(g) + O_2(g)$
Acidulated

7. Consider the following redox reaction and identify which element is oxidised and reduced both?

$$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

Hint P

8. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

Determine the correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+

Hint 2, 5 and 16 respectively.

9. Identify whether the following reaction is redox or not.

$$2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$$

Hint No

10. What products are expected from the disproportionation reaction of hypochlorous acid?

Hint $HClO_3$ and Cl_2O

11. What are the oxidation states of iodine in HIO_4, H_3IO_5 and H_5IO_6 respectively?

Hint +7, +7, +7

12. Identify whether the following redox reaction is correctly balanced or not.

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO + H_2O$$

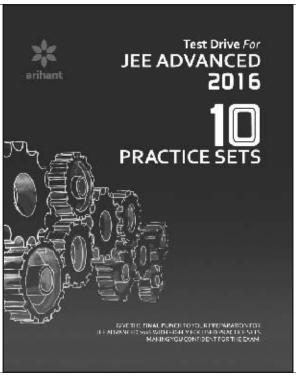
Hint No, correct balanced reaction is

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

13. Balance the following redox reaction,

$$MnCl_2 + PbO_2 + HNO_3 \longrightarrow HMnO_4 + PbCl_2 + Pb(NO_3)_2$$

Hint $2MnCl_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbCl_2 + 3Pb(NO_3)_2 + 2H_2O$



TARGET JEE 2016

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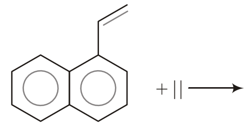
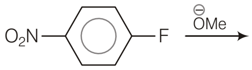
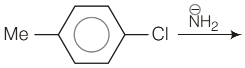
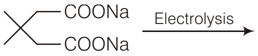
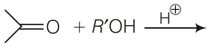
Questions to Measure Your Problem Solving Skills

1. Match the Column I (Reaction) with Column II (Reaction type).

	Column I		Column II
A.		p.	Addition elimination (ArSN)
B.		q.	Nucleophilic addition (NA)
C.		r.	Pericyclic reaction
D.		s.	Elimination addition (ArSN)
E.		t.	Rearrangement
F.		u.	Electrophilic addition (EA)

Codes

	A	B	C	D	E	F
(a)	p	s	u	q	r	t
(b)	r	p	s	t	u	q
(c)	s	u	t	p	q	r
(d)	t	q	r	s	p	u

2. Which of the following pair(s) is/are correctly matched?

I. Coloured but does not have unpaired electrons → $MnSO_4$

II. Electronic configuration of actinoids is not certain → energy difference is small in 5*f* and 6*d* energy levels.

III. *d*-block elements → Interstitial hydride.

IV. Alloys of transition elements → same atomic sizes.

(a) I and II *(b)* Only I *(c)* II, III and IV *(d)* III and IV

3. Two moles of a perfect gas undergo the following process.

I. A reversible isobaric expansion from (1 atm 20 L) to (1 atm 40 L).

II. A reversible isochoric change of state from (1 atm 40 L) to (0.5 atm 40 L).

III. A reversible isothermal compression from (0.5 atm 40 L) to (1 atm 20 L).

Calculate the total heat change involved in the above process.

(a) – 622.06 J

(b) 121.8 J

(c) 249.8 J

(d) 368.4 J

4. Fill in the blanks, using the correct option.

I. Passing H_2S into the mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates ...*A*... .

II. $NaX + MgCl_2 \xrightarrow[\text{(Boiling)}]{}$ White ppt. *X* is ...*B*... .

III. $X + H_2SO_4 \longrightarrow \underset{\substack{\text{Colourless gas}\\ \text{irritating smell}}}{Y} \xrightarrow{K_2Cr_2O_7/H^+}$ Green solution

X and *Y* are ...*C*... .

IV. The reagents NH_4Cl and $NH_3\,(aq)$ will precipitate ...*D*... .

	A	B	C	D
(a)	CuS and HgS	HCO_3^-	SO_3^{2-} and SO_2	Al^{3+}
(b)	MnS and CuS	NO_3^-	Cl^- and HCl	Ca^{2+}
(c)	MnS and NiS	CO_3^{2-}	S^{2-} and H_2S	Mg^{2+}
(d)	NiS and HgS	SO_4^{2-}	CO_3^{2-} and CO_2	Zn^{2+}

5. Fill in the blanks, using the correct option.

I. Coefficient of volume expansion of a gas is …*A*… .

II. …*B*… will have identical rate of effusion under similar conditions.

III. At the same temperature, the ratio of average velocity of SO_2 to CH_4 is …*C*… .

IV. At high pressure, van der Waals' equation becomes …*D*… .

	A	B	C	D
(a)	$\frac{1}{273}$	Dideuterium and helium	1 : 2	$pV = RT + pb$
(b)	$\frac{2}{273}$	Diprotium and dideuterium	2 : 3	$pV = RT - \frac{a}{V}$
(c)	$\frac{3}{273}$	Carbon dioxide and ethane	3 : 4	$pV = RT$
(d)	$\frac{4}{273}$	Ethene and ethane	1 : 6	$pV = RT + \frac{a}{V}$

6. Match the catalysts to the correct process.

Catalyst	Process
A. $TiCl_3$	p. Wacker process
B. $PdCl_3$	q. Ziegler-Natta polymerisation
C. $CuCl_2$	r. Contact process
D. V_2O_5	s. Deacon's process

Codes

	A	B	C	D
(a)	r	q	s	p
(b)	q	p	s	r
(c)	q	r	s	p
(d)	r	p	q	s

7. Consider to following statements.

I. $Ni(CN)_4$ is diamagnetic in nature.

II. $[Cr(NH_3)_6]^{3+}$ is expected to absorb visible light and shown colour.

III. $[Co(ox)_2(OH)_2]^-$ is exhibits highest paramagnetic behaviour.

IV. $[Co(NH_3)_6]^{3+}$ is an inner orbital complex and diamagnetic.

Choose the correct statements.

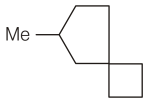
(a) I and II (b) Only III
(c) II and IV (d) All are correct

8. Calculate the percentage of HI dissociated when 0.96 g of it was heated to 450°C till equilibrium was reached. It was then quickly cooled and the amount of iodine liberated required 15.7 cm^3 of $\frac{N}{10}Na_2S_2O_3$.

(a) 0.75 (b) 20.9
(c) 7.85 (d) 0.78

9. Fill in the blanks, using the correct option.

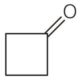
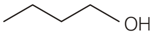
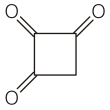
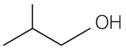
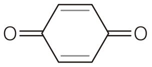
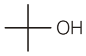
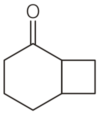
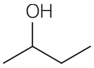
I. The IUPAC name of following spiro compound is …*A*… .



II. The volume of ozone formed, when two litre of air, i.e. 1915 mL of ozonised air is passed through Brodio's apparatus is …*B*… .

III. Tautomerism is not exhibited by …*C*… .

IV. …*D*… gives the most stable carbocation upon dehydration.

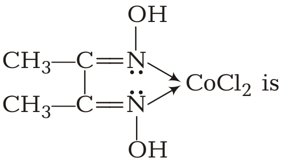
	A	B	C	D
(a)	2-methyl spiro [3.4] octane	225 mL		
(b)	3-methyl spiro [3.4] octane	85 mL		
(c)	6-methyl spiro [3.4] octane	170 mL		
(d)	7-methyl spiro [3.4] octane	42.5 mL		

10. Which of the following statements are correct? Choose the correct option.

I. EAN of Fe in $K_3[Fe(CN)_6]$ is 36.

II. Complex with bidentate ligands are called chelates.

III. IUPAC name of the following complex,



bis (dimethylglyoxime)dichlorocobalt (II).

IV. *M*(*ABCD*) shows *cis-trans* isomerism.

V. The existence of two different coloured complexes with the composition of $[Co(NH_3)_4Cl_2]^+$ is due to coordination isomerism.

(a) II and IV (b) I and III (c) II, IV and V (d) I, III and V

11. Fill in the blanks, using the correct option.

I. The isotopes of chlorine with mass number 35 and 37 exist in the ratio of …*A*… . Its average atomic mass is 35.5.

II. A compound of Na, C and O contain 0.0887 mole of Na, 0.132 mole of O and 2.65×10^{22} atoms of carbon. The empirical formula of the compound is …*B*… .

III. The vapour density of 5.6 L gas weighing 60 g at STP is ...*C*... .

IV. If repeated measurements give values close to one another, the number is ...*D*... .

	A	B	C	D
(a)	1 : 1	$Na_3C_5O_2$	60	Surely accurate
(b)	2 : 1	NaCO	30	Surely precise and accurate
(c)	3 : 2	Na_2CO_2	240	May be precise or accurate
(d)	3 : 1	Na_2CO_3	120	Surely precise

12. Which of the following statements are correct? Choose the correct option.

I. The half-life period of 1g sample with activity of 0.4 curie (atomic mass $=226$) is 1.2×10^{10} s. [Given, 1 curie $=3.7\times10^{10}$ dps]

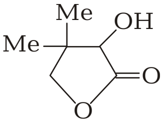
II. Bleeding is stopped by application of ferric chloride because ferric chloride seals the blood vessel.

III. Gelatin is added in manufacture of ice-cream in order to stabilise the colloid and prevent crystallisation.

IV. In the Haber process for synthesis of NH_3, molybdenum acts as catalyst and Fe as a promoter.

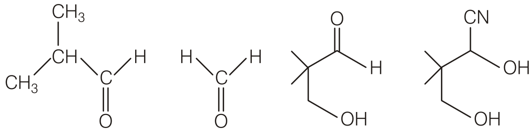
(a) Only III *(b)* II, III and IV *(c)* I, III and V *(d)* II and IV

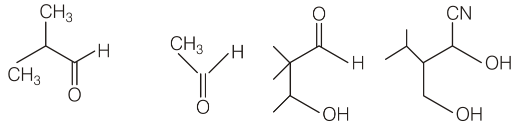
13. Two aliphatic aldehydes, (*P*) and (*Q*) react in the presence of *aq*.K_2CO_3 to give compound (*R*), which upon treatment with HCN gives compound(*S*). On acidification and heating, (*S*) gives

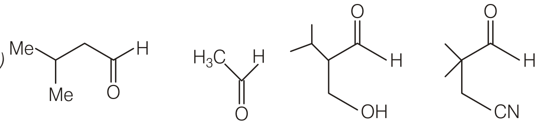


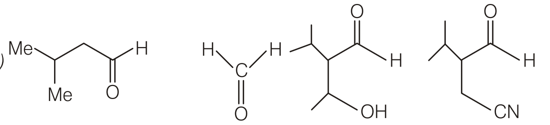
Identify the compounds *P*, *Q*, *R* and *S*.

P Q R S

(a)


(b)


(c)


(d)


14. Fill in the blanks, using the correct option.

I. Atomic radius of lithium (bcc structure), if edge length is 351 pm, is ...*A*... .

II. The edge length of unit cell of NaCl crystal with density 2.165 g/cm³ is ...*B*... .

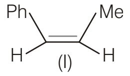
III. The edge length of cube containing one mole of NaCl ($d=2.165$ g/cm^3) is ...*C*... .

IV. Packing fraction of the element that crystallises in simple cubic arrangement is ...*D*... .

V. Number of unit cells present in 39 g of potassium (bcc structure) is ...*E*... .

	A	B	C	D	E
(a)	409 pm	6.02×10^{-8}cm	2.78 cm	$\pi/4$	N_A
(b)	151.98 pm	5.64×10^{-8}cm	3 cm	$\pi/6$	$0.5N_A$
(c)	154.15 pm	5.85×10^{-8}cm	2.89 cm	$\pi/3$	$N_A/4$
(d)	182 pm	5.98×10^{-8}cm	3.12 cm	$\pi/2$	$0.75N_A$

15. Match the Column I (Reaction) with Column II (Stereochemistry involved).

	Column I		Column II
A.	 $\xrightarrow[\text{NaBH}_4,\ \overset{\ominus}{\text{O}}\text{H}]{\text{Hg(OAc)}_2\ +\ \text{H}_2\text{O}}$	p.	*Syn*-hydration with *anti*-Markownikoff's regio specificity.
B.	(I) $\xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg (OCOCF}_3)_2\ +\ \text{PhOH}}$	q.	*Anti*-hydration with Markownikoff's regio selectivity.
C.	(I) $\xrightarrow[\text{(ii) H}_2\text{O}_2/\bar{\text{O}}\text{H}]{\text{(i) B}_2\text{H}_6/\text{THF}}$	r.	Cyclic intermediate transition state.
D.	Ph—≡—Me $\xrightarrow[\text{CH}_3\text{COOH}]{\text{B}_2\text{H}_6/\text{THF}}$	s.	Overall non-stereospecific.
		t.	Overall stereospecific.

Codes

	A	B	C	D
(a)	q,s	q,s	p,r,t	p,r,t
(b)	q,r	p,r,t	q,s	p,r,t
(c)	p,r,t	p,r,t	q,s	q,s
(d)	p,r	q	q,	r,t

16. The degree of dissociation of $Ca(NO_3)_2$ in a dilute solution containing 14 g of the salt per 200 g of water at 100°C is 70%. If the vapour pressure of water is 760 mm. The vapour pressure of solution is

(a) 785 mm *(b)* 769 mm *(c)* 746 mm *(d)* 753 mm

17. Choose the correct option after reading following information given below.

I. $(A)\,C_8H_{14} \xrightarrow[\text{Alk. KMnO}_4]{[\text{O}]} (B)+(C)+(D),$

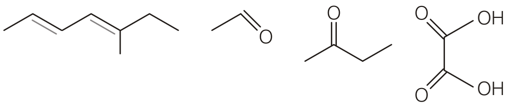
2 moles of H_2 is required for saturation of (*A*).

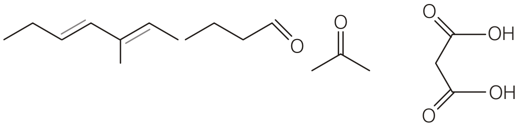
II. (*B*) reduces ammonical $AgNO_3$ and gives yellow colour with NaOH + I_2.

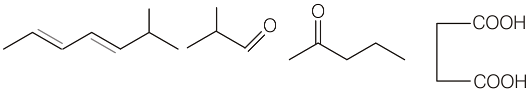
III. (*C*) does not reduce Tollen's reagent but gives iodoform test.

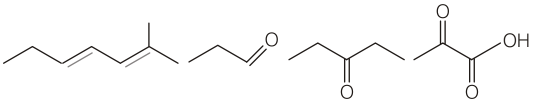
IV. (*D*) on dehydration with conc. H_2SO_4 gives mixture of colourless gases.

A B C D

(a) 

(b) 

(c) 

(d) 

18. Two first order reactions proceed at 25°C at the same rate. Find the ratio of rates of these reactions at 75°C, when temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3.

(*a*) 1 : 7.6 (*b*) 7.6 : 1 (*c*) 2 : 1 (*d*) 1 : 2

19. Which of the following statements is/are correct? Choose from the option.

I. Ozone is an allotrope of oxygen.

II. Hydrolysis of one mole of peroxodisulphuric acid produces two moles of peroxomono sulphuric acid.

III. Bond dissociation energy increases in the order: $I_2 < F_2 < Br_2 < Cl_2$.

IV. The ease of liquifaction of noble gases decrease in the order: Xe < Kr < Ar < Ne < He.

(*a*) I and II (*b*) III and IV (*c*) I and III (*d*) II and IV

20. Calculate the amount of current required to produce 85 g of H_2O_2 per hour during hydrolysis of ammonium persulphate. Which is produced during anodic oxidation of ammonium hydrogen sulphate, if the current efficiency is 60% and hydrolysis yield is 100%?

(*a*) 446.8 Å (*b*) 223.38 Å (*c*) 379.6 A (*d*) 146.2 A

21. Which of the following statements is/are incorrect? Choose the correct option.

I. Basic nature of oxides increases as $Al_2O_3 < MgO < Na_2O < K_2O$.

II. In silicon dioxide, each silicon and oxygen are bonded by double bonds and each silicon atom is surrounded by two oxygen atoms.

III. The number of P—O—P bonds in cyclic metaphosphoric acid is four.

IV. Out of the reagents,
NH_3 + CuO,
NH_4NO_3,
$(NH_4)_2Cr_2O_3$ and
$Ba(N_3)_2$ extra pure N_2 can be obtained by
NH_4NO_3.

(*a*) Only I (*b*) II, III and IV
(*c*) I and II (*d*) All of these

22. Which of the following statements are incorrect? Choose the correct option.

I. Solubility of AgCl is 1.31×10^{-5} M, when specific conductance of saturated solution of AgCl is 1.86×10^{-6} ohm^{-1} cm^{-1} and that of water is $6 \times 10^{-8} ohm^{-1}$ cm^{-1}, $(\Lambda^\circ_{AgCl} = 137.2$ ohm^{-1} $cm^2 eq^{-1})$.

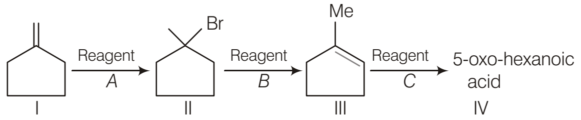
II. Equivalent conductance will be 4.6 ohm^{-1} cm^{-1} eq^{-1}, when resistance of 1N solution of CH_3COOH is 250 ohm.
(Cell constant = 1.15 cm^{-1}).

III. $Ag(s)/AgNO_3(0.01M) || AgNO_3(0.05M)/Ag(s)$. The emf of cell is – 0.0414 V.

IV. $2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(s)$. The value of $E^\circ_{Fe^{3+}/Fe^{2+}}$ is 0.77V.
(Given, $E^\circ_{I_2/I^-} = +0.54$ V, $K_{eq} = 10^8$ at 298 K).

(*a*) I and II (*b*) III and IV
(*c*) I and III (*d*) II and IV

23. Complete the reaction. Choose the correct option.



	A	B	C
(*a*)	HBr	high temperature	O_3/H_2O_2
(*b*)	HBr + *ROOR* + *hν*	CH_3O^- + high temperature	O_3/Ph_3P
(*c*)	HI	EtO^- + high temperature	$O_3/NaBH_4$
(*d*)	HCl + *ROOR*	CsOH + C_2H_5OH	$KMnO_4/\bar{O}H$

24. Which of the following statements are true? Choose the correct option.

I. Lattice energy decreases in the order as LiF > LiCl > LiBr > LiI.

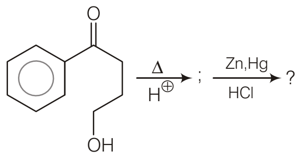
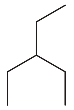
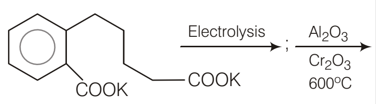
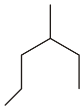
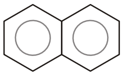
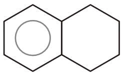
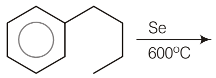
II. Acidified solution of chromic acid on treatment with H_2O_2 yield blue solution of CrO_3.

III. Ionic radii increase in magnitude as atomic number of alkali metals increases.

IV. The activity of alkaline earth metals as reducing agents decreases from Be to Ca and increases from Ca to Ba.

(*a*) I and III (*b*) II and IV
(*c*) I and IV (*d*) II and III

25. Match the Column I (Reactants) with Column II (Products).

Column I	Column II
A. 	p. 
B. 	q. 
C. Di-(3-pentyl) lithium cuperate $\xrightarrow{C_2H_5Br}$	r. 
D. Di-(2-pentyl) lithium cuperate $\xrightarrow{C_2H_5Br}$	s. 
E. 	

Codes

	A	B	C	D	E
(a)	r	s	q	p	r
(b)	q	s	p	s	r
(c)	s	r	p	q	r
(d)	p	q	r	r	s

26. Fill in the blanks, using the correct option.

I. pH changes from ...*A*... to ...*B*... upon ten-fold dilution of 0.1 M NH_4Cl. ($K_b = 1.8 \times 10^{-5}$)

II. pH of 0.02M NH_4Cl (*aq*) equal to ...*C*... ($pK_b = 4.73$)

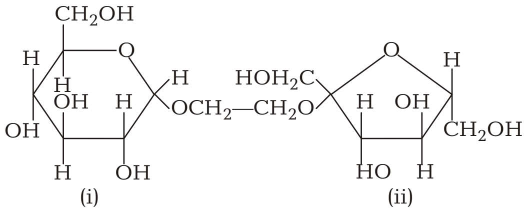
III. Degree of hydrolysis of ...*D*... (salt) is independent of concentration of salt solution.

IV. pH of 1M $PO_4^{3-}(aq)$ solution will be ...*E*... ($pK_b[PO_4^{3-}] = 1.62$).

	A	B	C	D	E
(a)	5.128	5.627	5.48	CH_3COONH_4	13.19
(b)	2.87	3.37	3.78	CH_3COONa	12.38
(c)	1.00	2.00	4.73	NH_4Cl	1.62
(d)	5.48	6.48	7.00	NaCl	7

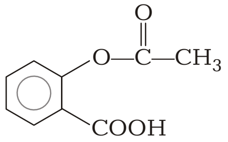
27. Fill in the blanks, using the correct option.

I. The disaccharide



is ...*A*... .

II. The weakest intermolecular forces of attraction are found in ...*B*... (polymer).

III. 

is used as ...*C*... .

IV. Smog is essentially caused by presence of ...*D*... .

	A	B	C	D
(a)	Ring (i) is pyranose with α-glycosidic link	Natural rubber	Analgesic	Oxides of N and S
(b)	Ring (i) is furanose with α-glycosidic link	Nylon	Anti inflammetory	O_3 and N_2
(c)	Ring (ii) is furanose with α-glycosidic link	Cellulose	Hypnotic	O_2 and N_2
(d)	Ring (ii) is pyranose with β-glycosidic link	PVC	Antiseptic	O_2 and O_3

28. At 700K, 0.45 mole of CO_2 and 0.45 mole of H_2 reacts to form CO and H_2O at equilibrium ($K_C = 0.11$). After equilibrium is reached, another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. The composition of the mixture (CO_2, CO) at the new equilibrium state is

(a) 0.594, 0.196 (b) 0.34, 0.11 (c) 0.196, 0.594 (d) 0.11, 0.34

29. In which of the following hybridisation of central atom(s) is not affected?

(a) PCl_5 solid dissociates into PCl_4^+ and PCl_6^-
(b) NH_3 is protonated to give NH_4^+
(c) NH_4NO_3 is heated to give N_2O
(d) LiH reacts with AlH_3 and forms $LiAlH_4$

30. Which of the following statements is/are true? Choose the correct option.

I. Energy of radiation emitted for electronic transition from infinite to stationary state of H-atom is 2.17×10^{-18} J.

II. Velocity of an electron placed in the third orbit of H-atom is 0.729×10^8 cm/s.

III. The electron of the first Bohr's orbit of H-atom goes around 6.59×10^{15} times in one second.

(a) Only I
(b) II and III
(c) All of these
(d) None of these

Answers

1. (b)	**2.** (c)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (d)	**8.** (b)	**9.** (c)	**10.** (a)
11. (d)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (c)	**17.** (a)	**18.** (b)	**19.** (c)	**20.** (b)
21. (b)	**22.** (b)	**23.** (a)	**24.** (a)	**25.** (c)	**26.** (a)	**27.** (a)	**28.** (a)	**29.** (b)	**30.** (c)

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Questions to Measure Your Problem Solving Skills

1. Which of the following statements are correct? Choose the correct option.

I. Dissolution of a non-volatile solute into a liquid leads to a decrease in tendency of the liquid to freeze.

II. The vapour pressure of the solution remains constant, when increasing amounts of a solid HgI_2 is added to aqueous solution of NaI.

III. A liquid possessing low freezing point and high enthalpy of freezing will be most suitable for determining the molecular mass of a compound by cryoscopic measurement.

IV. A mixture of two immiscible liquids at a constant pressure of 1 atm boils at temperature smaller than the normal boiling point of either liquids.

(a) I and IV *(b)* II and III
(c) I and II *(d)* III and IV

2. A mixture contains CO_3^{2-}, SO_3^{2-} and SO_4^{2-}. Scheme is provided but in disordered form. Arrange the scheme and choose the correct option.

I. Add dil. HCl.

II. Pass the evolved gas into the lime water.

III. Add dil. HCl and $BaCl_2$.

IV. Add $K_2Cr_2O_7$.

(a) I, IV, II then III *(b)* I, II, III then IV
(c) II, I, III then IV *(d)* IV, III, I then II

3. Which of the following statements are correct? Choose the correct option.

I. Nylon fibres have lower tensile strength than terylene fibres.

II. In terylene, there is weak dipole-dipole interaction while in nylon, there is strong intermolecular H-bonding.

III. Novolac is prepared when $\frac{P}{F} < 1$ and bakelite is prepared when $\frac{P}{F} > 1$.

IV. Novolac is used in manufacture of adhesives and bakelite is used for making switches and plugs.

(a) II and III *(b)* I and III *(c)* I and II *(d)* III and I

4. Which of the following statements is/are incorrect? Choose the correct option.

I. *t*-butyl ethanoate can be prepared by the reaction of CH_3COOH and Me_3C ¾ Br in basic medium.

II. HCl cannot be used for conversion of *R*COOH to *R*COCl.

III. Esters can be prepared more efficiently by the sequence,
R ¾ COOH ¾→ *R*COCl ¾→ *R*COOR′ rather than *R*COOH ¾→ *R*COOR′.

IV. Acyl azides are more reactive than *R*COCl but less reactive than anhydrides.

(a) II and III *(b)* I and IV *(c)* I, II and III *(d)* Only IV

5. Match the Column I with Column II.

	Column I		Column II
A.	$Fe^{3+}(Fe^{2+}\ Fe^{3+})O_4$	p.	Rutile structure
B.	$Mg^{2+}Al_2^{3+}O_4$ and $CO^{2+}(CO^{3+})_2O_4$	q.	Inverse 2 : 3 spinel structure
C.	MnO_2 and SnO_2	r.	Normal 2 : 3 spinel structure
D.	$BaTiO_3$	s.	Perovskite structure
E.	CaF_2 and $SrCl_2$	t.	Fluorite type structure

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	s	t	q	p	r	*(b)*	q	r	p	s	t
(c)	q	r	p	s	t	*(d)*	r	q	s	p	t

6. Two second order reactions *A* and *B* have identical frequency factors. Activation energy of *A* exceeds that of *B* by 10.46 kJ/mol. At 100°C, the reaction *A* is 30% completed after 60 min, when initial concentration is 0.1 mol/dm^3. How long will it take reaction *B* to reach 70%, completion at the same temperature of an initial concentration of 0.05 mol/dm^3?

(a) 13.4 min *(b)* 22.4 min *(c)* 16.7 min *(d)* 28.2 min

7. Which of the following statements are correct? Choose the correct option.

I. Pb can be obtained by reduction of roasted ore with coke.

II. SnO_2 can be used to concentrate tin stone.

III. Tin stone is amphoteric.

IV. Scrap tin plate can be recycled by dissolving tin in NaOH solution followed by electrolysis.

(a) I and II *(b)* III and IV
(c) I and III *(d)* All of these

8. $MeCH_2COOH \xrightarrow[\substack{CH_2N_2 \\ Ag_2O/Pt}]{SOCl_2} B \xrightarrow{H_2O} C$

Which of the following statements are incorrect about the given reaction? Choose the correct option.

I. The products *B* and *C* respectively are $MeCH{=}C{=}O$ and $MeCH_2COOMe$.

II. The reaction proceeds *via* the formation of acyl carbene $MeCO\ddot{C}H$ as the intermediate species.

III. The compound *B* on reaction with $MeNH_2$ forms the product $MeCH_2CH_2CONHMe$.

IV. The compound *B* on reaction with MeOH forms the product $MeCH_2CH_2COOMe$.

(a) I and II *(b)* III and IV *(c)* II and III *(d)* I and IV

9. The standard reduction potential data at 25°C is given below.

$E°_{(Fe^{3+}/Fe^{2+})} = +0.77V$; $E°_{(Fe^{2+}/Fe)} = -0.44V$

$E°_{(Cu^{2+}/Cu)} = +0.34V$; $E°_{(Cu^{+}/Cu)} = +0.52V$

$E°, O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O = +1.23V$

$E°, O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH = +0.40V$

$E°_{(Cr^{3+}/Cr)} = -0.74$; $E°_{(Cr^{2+}/Cr)} = +0.91V$

Match the Column I (Redox pair) with Column II ($E°$ values).

	Column I	Column II
A.	$E°_{(Fe^{3+}/Fe)}$	p. – 0.18 V
B.	$E° (4H_2O \rightleftharpoons 4H^+ + 4\bar{O}H)$	q. – 0.40 V
C.	$E° (Cu^{2+} + Cu \longrightarrow 2Cu^+)$	r. – 0.04 V
D.	$E°_{(Cr^{3+}, Cr^{2+})}$	s. – 0.83 V

Codes

	A	B	C	D		A	B	C	D
(a)	s	p	q	r	*(b)*	q	r	s	p
(c)	p	q	r	s	*(d)*	r	s	p	q

10. Which of the following statements are correct? Choose the correct option.

I. On adding Cl_2 water to solution of starch and KI, it turns blue.

II. Bleaching action of SO_2 is unstable while that of Cl_2 is stable.

III. Nitrous oxide is more helpful in combustion than air.

IV. Ge and Sn are reducing agents, while Pb is an oxidising agent.

(a) I and II
(b) III and IV
(c) All of the above
(d) None of the above

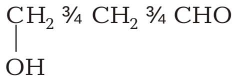
11. Identify *B* and *E*. Choose the correct option.

$$CH_3CHO \xrightarrow{HCHO + \overset{\ominus}{O}H} B \xrightarrow{HCHO + \overset{\ominus}{O}H} C \xrightarrow{HCHO + \overset{\ominus}{O}H} D \xrightarrow{HCHO + \overset{\ominus}{O}H} E + HCO\overset{\ominus}{O}$$

I. $(HOCH_2)_3C-CHO$

II. $C(CH_2OH)_4$

III. $CH_2{=}CH-CHO$

IV. 
$\underset{\displaystyle OH}{\underset{|}{CH_2}}-CH_2-CHO$

(a) I and III *(b)* II and IV *(c)* I and IV *(d)* II and III

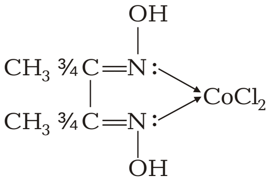
12. A hydrogen electrode and a calomel half-cell are used to determine the pH of a solution on a mountain top where the pressure is 500 mm of Hg. The pressure was wrongly assumed to be 760 mm of Hg and pH was found to be 4. What is the correct pH?

Cell: $H_2(g)$/solution || KCl, Hg_2Cl_2/ Hg

(a) 4.09 *(b)* 3.92 *(c)* 3.75 *(d)* 4.25

13. Fill in the blanks with appropriate options. Choose the correct option.

I. The IUPAC name of the complex

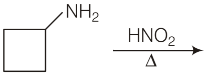
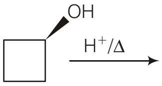
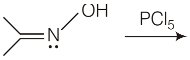
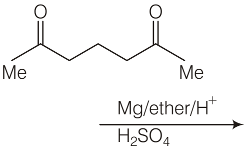


is …*A*…

II. …*B*… cannot show linkage isomerism.
III. …*C*… exhibits optical isomerism.
IV. …*D* … forms a π-complex.

	A	B	C	D
(a)	Dichlorodimethylglyoximatocobalt (II)	NH_3	*cis*-$[Co(en)_2Cl_2]$	Ferrocene
(b)	*Bis*-(dimethylglyoxime) dichlorocobalt (II)	$NO_2^{\ominus}$	*trans*-$[Co(en)_2Cl_2]$	Trimethyl aluminium
(c)	Dimethylglyoximecoba-lt (II) chloride	$SCN^{\ominus}$	*trans*-$[Pt(NH_3)_2Cl_2]$	Diethyl zinc
(d)	Dichlorodimethylglyoxime-N, N-cobalt (II)	$CN^{\ominus}$	*cis*-$[Pt(NH_3)_2Cl_2]$	Nickel carbonyl

14. Match the Column I (Reaction) with Column II (Mechanism). Choose the correct option.

	Column I	Column II
A.		p. Ring expansion
B.		q. Ring contraction
C.		r. Carbocation
		s. Rearrangement
D.		t. Radical anion

Codes

	A	B	C	D
(a)	p, r, s	r, s, t	q, r, s	s
(b)	q, r, s	p, r, s	s	r, s, t
(c)	r, s, t	q, r, s	p, r, s	p, s, t
(d)	p, s, t	q, s, t	q, r, s	s

15. The following solutions are mixed, 500 mL of 0.01 M $AgNO_3$ and 500 mL solution that was both 0.01 M in NaCl and 0.01 M in NaBr. Given, $K_{sp}(AgCl) = 10^{-10}$; $K_{sp}(AgBr) = 5\times10^{-13}$. Consider the following statements and mark them as True (T) or False (F). Choose the correct option.

I. AgCl does not precipitate.

II. $[Cl^-]_{equil.} = 5\times10^{-3}$ M

III. $[Ag^+]_{equil.} = 2.5\times10^{-8}$ M

IV. $[Br^-]_{equil.} = 2.0\times10^{-5}$ M

	I	II	III	IV		I	II	III	IV
(a)	T	F	T	T	*(b)*	F	T	F	F
(c)	T	T	F	F	*(d)*	T	F	T	F

16. Which of the following statements are correct? Choose the correct option.

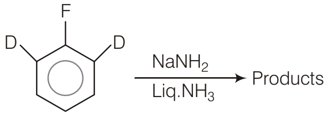
I. Magnetic moment of $[Fe(H_2O)_6]^{2+}$ is 4.9 BM, while that of $[Fe(CN)_6]^{4-}$ is zero.

II. $[Co(NH_3)_6]^{3+}$ is an inner orbital complex, while $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

III. $[Fe(CN)_6]^{3-}$ is weakly paramagnetic, while $[Fe(CN)_6]^{4-}$ is diamagnetic.

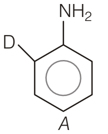
IV. $NH_2{\times}NH_2$ although possesses two electron pair for donation but does not act as chelating agent.

(a) I and II *(b)* III and IV
(c) I, II and III *(d)* All of these

17. 

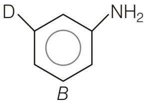
Which of the following statements are correct for the above reaction? Choose the correct option.

I. The product is a mixture of



A

and



B

II. The product *B* is a cine-substitution product.

III. The reaction proceeds *via* benzyne intermediate.

IV. The reaction is ArSN (addition-elimination).

(a) I, II and III *(b)* II and III *(c)* Only III *(d)* Only IV

18. A 6.25g sample of NH_4Cl is placed in an evaluated 4.0 L container at 27°C. After equilibrium the total pressure inside the container is 0.820 bar and some solid remain in the container.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

Which of the following statements are correct? Choose the correct option.

I. The value of K_p for the reaction is 0.168.

II. The amount of solid NH_4Cl left behind in the container at equilibrium is 2.856 g.

III. If the volume of container was doubled at constant temperature, amount of solid in the container decreases.

IV. The extent of decomposition can be increased by increasing the temperature.

(a) I and II *(b)* III and IV
(c) I, II, III and IV *(d)* None of these

19. Fill in the blanks. Choose the correct option.

Uranium ($^{238}_{92}U$) decayed to $^{206}_{82}Pb$. The decay process is ${}_{92}U^{238} \xrightarrow{(x\alpha,\ y\beta)} {}_{82}Pb^{206}$; $t_{1/2} = 4.5\times10^9$ yrs.

I. x and y in the above decay series are ...*A*... .

II. The age of the rock containing equal amounts of ^{238}U and ^{206}Pb is ...*B*... .

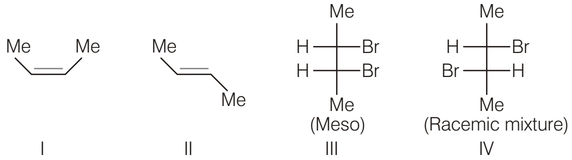
III. Packing fraction of ^{238}U with atomic mass 238.125 amu is ...*C*...

IV. The analysis of rock shows the relative number of U^{238} and Pb^{206} atoms (Pb/U = 0.25). The age of rock will be ...*D*... .

	A	B	C	D
(a)	6 and 8	9×10^9 yrs	6.25	$\frac{2.303}{0.693} \times 4.5 \times 10^9 \log 0.25$
(b)	9 and 6	13.5×10^9 yrs	0.125	$\frac{2.303}{0.693} \times 4.5 \times 10^9 \log 4$
(c)	8 and 8	2.25×10^9 yrs	12.5	$\frac{2.303}{4.5 \times 10^9} \times 0.693 \log 4$
(d)	8 and 6	4.5×10^9 yrs	5.25	$\frac{2.303}{0.693} \times 4.5 \times 10^9 \log 1.25$

20. $$Me-C\equiv C-Me \xrightarrow{Cs+EtOH} A \xrightarrow{Br_2} D$$
$$\xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } BH_3 + THF} B \xrightarrow{Br_2} E$$
$$\xrightarrow[CH_3COOH]{Si_2BH} C \xrightarrow{Br_2} F$$

Products *A*, *B*, *C*, *D*, *E* and *F* repectively are



Codes

	A	B	C	D	E	F
(a)	I	II	I	IV	III	IV
(b)	I	I	II	IV	IV	III
(c)	II	I	I	IV	III	III
(d)	II	I	I	III	IV	IV

21. Find out the correct value of x in the statements given below. Choose the correct option.

I. Bond dissociation energy of XY, X_2, Y_2 (all diatomic molecules) are in the ratio 1 : 1 : 0.5 and ΔH_f of XY is -100 kJ/mol. The bond dissociation energy of X_2 is 100x.

II. $\Delta_f H°$ of hypothetical MgCl is -125 kJ/mol and for $MgCl_2$ is -642 kJ/mol. The enthalpy of disproportionation of MgCl is -49x.

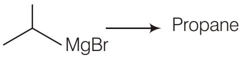
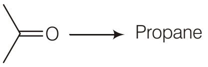
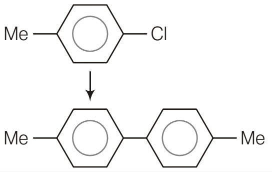
III. The lattice energy of solid KCl is 181 kcal/mol and enthalpy of solution of KCl in H_2O is 1.0 kcal/mol. If the hydration enthalpies of K^+ and Cl^- ions are in ratio 2 : 1, then enthalpy of hydration of K^+ is -20x kcal/mol.

IV. A heated iron block at 127°C loses 300 J of heat to the surroundings which are at a temperature of 27°C. This process is 0.05x J/K.

Codes

	I	II	III	IV
(a)	8	4	5	6
(b)	4	8	6	5
(c)	6	5	4	8
(d)	5	6	8	4

22. Match the Column I with Column II.

	Column I	Column II
A.		p. Zn–Hg | conc. HCl
B.		q. B_2H_6 + Ether + CH_3COOH
C.		r. Propanoic acid
D.		s. $NH_2-NH_2 + C_2H_5O^-$ t. P + HI u. Cu + Δ

Codes

	A	B	C	D
(a)	p, q	r, s	t	u
(b)	p	q, r	s	t, u
(c)	r	p, s, t	q	u
(d)	s, t	q, u	p	r

23. Two flasks *A* and *B* have equal volumes. *A* is maintained at 300 K and *B* at 600 K, while *A* contains H_2 gas, *B* has an equal mass of CH_4 gas. Assuming ideal behaviour for both the gases, identify the correct statements.

I. Greater number of molecules are present in flask *B*.

II. High pressure is attained in flask *A*.

III. Compressibility factor of both the flasks is same.

IV. Total kinetic energy is same in both the flasks.

V. Molar kinetic energy is greater for flask *B*.

VI. Molecules are travelling with the same speed in both flasks.

Mark the statements as True (T) or False (F).

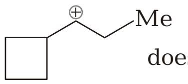
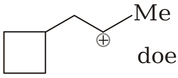
	I	II	III	IV	V	VI
(a)	F	F	F	F	F	F
(b)	T	T	T	T	T	T
(c)	T	F	F	T	F	T
(d)	F	T	T	F	T	F

24. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

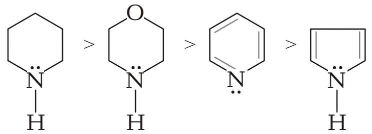
$$XeF_6 \xrightarrow[\text{hydrolysis}]{\text{Complete}} P + \text{Other products} \xrightarrow[H_2O]{\bar{O}H} Q$$
$$\xrightarrow{\text{Slow disproportionation in } HO^-/H_2O} \text{Products}$$

(a) 0 *(b)* 1 *(c)* 2 (d) 3

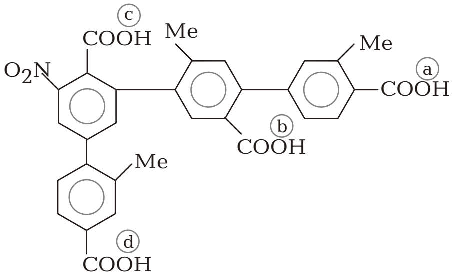
25. Which of the following statements are incorrect? Choose the correct option.

I.  does not undergo ring expansion but  does.

II. Order of decreasing basic character is



III. Decreasing order of acidic character is $c < a < d < b$,



IV. Alkyl group acts as electron donor, when attached to a π-system.

(a) II and IV *(b)* I and III *(c)* I and II *(d)* III and IV

26. 40 mL 0.05 M solution of sodium sesquicarbonate dehydrate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is titrated against 0.05 M HCl solution, x mL of acid is required to reach the phenolphthalein end-point, while y mL of same acid was required when methyl orange indicator was used in a separate titration. Which of the following statements are correct? Choose correct option.

I. $y - x = 80$ mL II. $y + x = 160$ mL

III. If the titration is started with phenolphthalein indicator and methyl orange is added at the end-point, 2x mL of HCl would be required further to reach end-point.

IV. If the same volume of same solution is titrated against 0.10 M NaOH, x/2 mL of base would be required.

(a) I and II *(b)* III and IV *(c)* I, II and III *(d)* All of these

27. Which series of reactions correctly represents chemical relations related to iron and its compound?

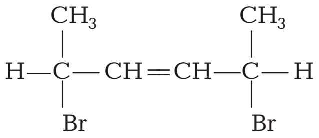
(a) $Fe \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe$

(b) $Fe \xrightarrow{O_2, \text{ Heat}} FeO \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{\Delta} Fe$

(c) $Fe \xrightarrow{Cl_2, \text{ Heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{Zn} Fe$

(d) $Fe \xrightarrow{O_2, \text{ Heat}} Fe_3O_4 \xrightarrow{\text{CO, 600°C}} FeO \xrightarrow{\text{CO, 700°C}} Fe$

28. Which of the following statements are correct about the given below compound? Choose the correct option.



$$H-\underset{Br}{\overset{CH_3}{C}}-CH{=}CH-\underset{Br}{\overset{CH_3}{C}}-H$$

I. The total number of stereoisomers possible for the compound is 6.

II. The total number of diastereomers possible for the compound is 3.

III. If the stereochemistry about the double bond in the compound is *trans* the number of enantiomers possible for the compound is 4.

IV. If the stereochemistry about the double bond in the compound is *cis*, the number of enantiomers possible for the compound is 2.

(a) I and IV *(b)* II and III
(c) I and III *(d)* II and IV

29. Which of the following statement is incorrect? Choose the correct option.

I. Presence of orbitals within a subshell is proved by Zeeman effect.

II. Bohr's atomic model is against Heisenberg's uncertainty principle.

III. Bond length decreases when N_2^+ is formed from N_2 but increases when O_2^+ is formed from O_2.

IV. BF_3 and graphite, both are sp^2 hybridised. BF_3 is bad conductor and graphite is good conductor of electricity.

(a) Only IV *(b)* Only III
(c) Only II *(d)* Only I

30. Which of the following statements are correct? Choose the right option.

I. Acid rain water have a pH normally about 7.6.

II. The process of adsorption is always exothermic.

III. Mutarotation of β-D-glucopyranose faster in the presence of 2-pyridinol.

IV. 5 moles of SO_3^{2-} reacts with 2 moles of $KMnO_4$ in acidic medium.

(a) I and II *(b)* III and IV
(c) I, II and III *(d)* I, III and IV

Answers

1. (a)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (c)	**6.** (b)	**7.** (d)	**8.** (a)	**9.** (d)	**10.** (c)
11. (b)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (d)	**17.** (a)	**18.** (c)	**19.** (d)	**20.** (d)
21. (b)	**22.** (c)	**23.** (d)	**24.** (c)	**25.** (b)	**26.** (d)	**27.** (d)	**28.** (a)	**29.** (b)	**30.** (d)

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Questions to Measure Your Problem Solving Skills

Paper 1

One or More than One Options Correct Type

1. Choose the correct options from the following.

(a) Cyclopentadiene is much more acidic than 1, 3-cyclohexadiene

(b) Cyclopropenyl cation is the smallest aromatic substance

(c) H of the CH_2 group in cycloheptatriene is much more acidic than a typical allylic H

(d) Cyclopentadienyl cation is a diradical

2. Consider the geometrical isomer(s) of PBr_2Cl_3 molecule and choose the correct options from the following.

(a) There are three geometrical isomers and all have zero dipole moment

(b) There are three geometrical isomers and two of them have same dipole moment

(c) Bigger atoms are far apart in the structure so that dipole moment becomes zero

(d) There is involvement of bent rule

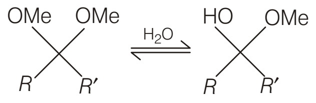
3. ΔG_f° for the formation of HI(g) from its gaseous elements is –10.10 kJ/mol at 500 K. When the partial pressure of HI is 10.0 atm and that of I_2 is 0.001 atm, the partial pressure of dihydrogen at this temperature would be to reduce the magnitude of ΔG for the reaction to zero

(a) 700 atm *(b)* 70 atm

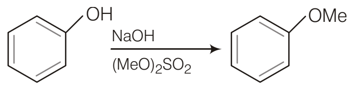
(c) 775 atm *(d)* 77 atm

4. Which of the following reactions show(s) S_N1 mechanism?

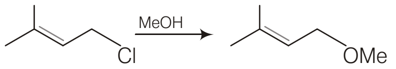
(a)



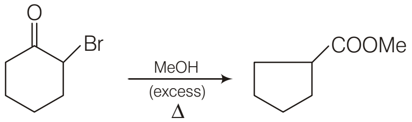
(b)



(c)



(d)



5. Consider the following complex compounds $\underset{\text{I}}{[Ir(CO)Cl(PPh_3)_2]}$ and $\underset{\text{II}}{[Mn(CN)_6]^{4-}}$ and choose the correct option(s) from the following.

(a) CO and CN act as π-accepting ligands

(b) Magnetic moment of metal ion in II is 1.73 BM

(c) Both I and II follow 18 electron rule

(d) Both I and II show characteristic colour

6. At 50°C the vapour pressure of pure CS_2 is 854 torr. A solution of 2.0 g of sulphur in 100 g of CS_2 has a vapour pressure of 848.9 torr.

Choose the correct choices from the following.

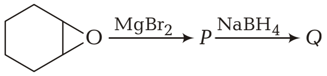
(a) Formula of the sulphur molecule is S_8

(b) Formula of the molecule is C_2S_2

(c) Molality of sulphur molecule is 0.079 m

(d) Mole fraction of CS_2 is found out by Raoult's law

7.



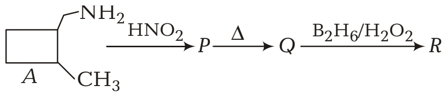
(a) $MgBr_2$ activates the epoxide

(b) P is an ester while Q is an acid

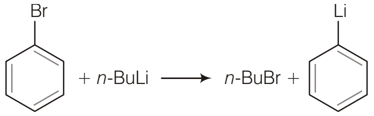
(c) P and Q are strained aldehyde and alcohol respectively

(d) P undergoes nucleophilic addition reaction readily, while Q readily undergoes dehydration upon heating

8. Choose the correct option from the following.
(a) The fluoro derivative of diazene are more stable than diazene
(b) Oxidation of hydrazine is an endothermic reaction
(c) Hydrazine is an oxidising agent in basic medium
(d) Phosphine has stronger intermolecular attraction than ammonia in solid state

9. 

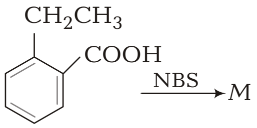
(a) *P*, *Q* and *R* are cyclic alcohols
(b) *P* and *R* are cyclic alcohols, while *Q* is unsubstituted alkene
(c) *P* and *R* are cyclic ester, while *Q* is open chain alkene
(d) Step *A* to *P* : Diazotisation
P to *Q* : Dehydration
Q to *R* : Hydroboration-oxidation

10. Select the correct reaction(s) from the following.
(a) $[CH_3Hg(H_2O)]^+ + BH^+ \rightleftharpoons [CH_3HgB]^+ + H_3O^+$
(b) $[CH_3Hg(H_2O)]^+ + SH^- \rightleftharpoons [CH_3HgSH]^- + H_3O^+$
(c) $[CH_3Hg(H_2O)]^+ + HSCN \rightleftharpoons CH_3HgSCN + H_3O^+$
(d) 

Single Integer Type

11. The same quantity of electricity that liberated 2.158 g silver was passed through a solution of a gold salt and 1.314 g gold was deposited. The equivalent weight of silver is 107.9. What is the oxidation state of gold in this gold salt?

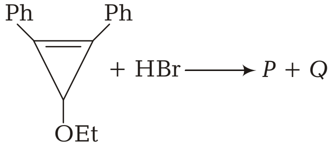
12. How many P—O—P bond(s) present in cyclotrimetaphosphoric acid?

13. 

Calculate the number of conjugated double bonds in the product *M*.

14. An electron in a hydrogen atom in its ground state absorbs 1.50 times as much energy as the minimum required for it to escape from the atom. The value of the emitted electron can be calculated in the form of $x \times 10^{-10}$ m, where x is approximate value.

15. $SeOCl_2$ has pyramidal structure with Cl—Se—Cl angle is 97°. How many double bonds causing the distortion in the structure?

16. 

How many active hydrogens are present in the product *P*?

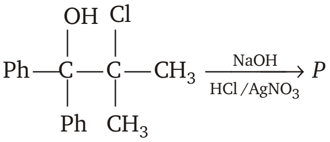
17. Calculate the per cent error in the hydronium ion concentration made by neglecting the ionisation of water in a 1.0×10^{-6} M NaOH solution.

18. $2H—\equiv—H \xrightarrow[NH_4Cl]{CuCl} A \xrightarrow{H_2 + Ni_2B} B$

$B \xrightarrow{Br_2} C$ (major)

How many allylic hydrogen present in the major product of this reaction?

19. 20% surface sites have absorbed N_2. On heating N_2 gas is evolved from sites and were collected at 0.001 atm and 298 K in a container of volume 2.46 cm^3. Density of surface sites is $6.023 \times 10^{14}/cm^3$ and surface area is 1000 cm^2. Find out the number of surface sites occupied per molecule of N_2.

20. 

$$Ph—\overset{OH}{\underset{Ph}{C}}—\overset{Cl}{\underset{CH_3}{C}}—CH_3 \xrightarrow[HCl/AgNO_3]{NaOH} P$$

A

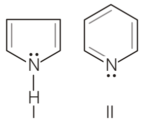
How many hydrogen atom(s) in product *P* can participate in tautomerism?

Paper 2

Single Option Correct Type

1. Bio-chemists often define Q_{10} for a reaction as the ratio of the rate constant at 37°C to the rate constant at 27°C. The energy of activation for a reaction that has a Q_{10} of 2.5 must be
(a) 7.1 kJ/mol
(b) 71 kJ/mol
(c) 7100 kJ/mol
(d) 51.7 kJ/mol

2. Consider the following compounds and choose the correct option from the following.



(a) I is antiaromatic whereas II is aromatic
(b) I is less basic than II
(c) Both undergo electrophilic reaction at C-2 position
(d) I is easily protonated than II

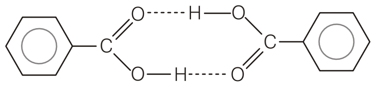
3. Sulphur reacts with chlorine in 1 : 2 ratio and forms X. Hydrolysis of X gives a sulphur compound Y. The hybridisation of S-atom in Y is

(a) sp *(b)* sp^3d

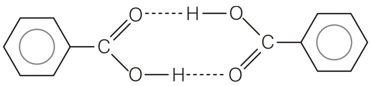
(c) sp^3 *(d)* sp^2

4. A certain solution of benzoic acid in benzene has a freezing point of 3.1°C and a normal boiling point of 82.6°C. The structure of solute particles at the two temperatures would be

(a)



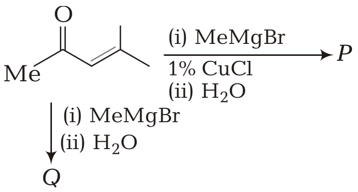
(b)



(c) Both (a) and (b)

(d) None of the above

5.



Choose the correct choice from the following.

(a) Q is formed through conjugate addition

(b) P is formed through conjugate addition

(c) Catalyst provide the path of direct addition

(d) None of the above

6. Hydrogen peroxide when reacts with KIO_4 and NH_2OH separately. What type of behaviour it shows with respect to these reagents?

(a) Reducing agent and oxidising agent

(b) Reducing agent and reducing agent

(c) Oxidising agent and oxidising agent

(d) Oxidising agent and reducing agent

7. 1, 3, 5-trihydroxy benzene reacts with H_2NOH to give an oximino derivative, whereas phenol does not react because

(a) phenol does not give tautomer

(b) tautomer of 1, 3, 5-trihydroxy benzene is stable

(c) tautomer of 1, 3, 5,-trihydroxy benzene has sufficient concentration in the phenol-keto equilibrium

(d) None of the above

8. The correct statement for orthoboric acid is

(a) it behaves as strong electrolyte in water

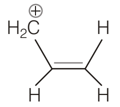
(b) acidity of its aqueous solution increases upon addition of ethylene glycol

(c) it has a 3-D structure due to H-bonding

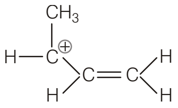
(d) it behaves as a weak acid in water due to self ionisation

9. Which one of the following intermediate undergoes the fastest S_N1 reaction?

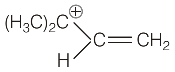
(a)



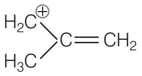
(b)



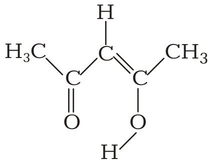
(c)



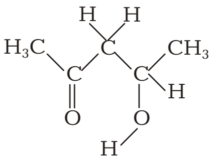
(d)



10.



I



II

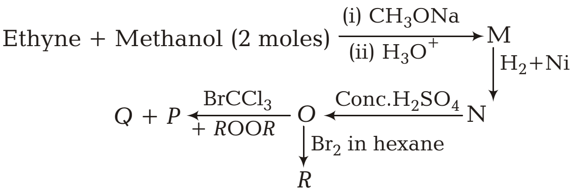
Which one of the above molecule is likely to form more stable H-bonds?

(a) Only I *(b)* Both I and II

(c) Only II *(d)* None of these

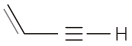
Paragraph-I (For Q.Nos. 11 and 12)

In the following reaction sequence, M to R are formed.

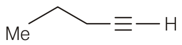


11. Product O is

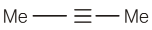
(a)



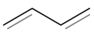
(b)



(c)



(d)



12. How many halogen group(s) are present in the product R?

(a) Zero *(b)* One *(c)* Two *(d)* Three

Paragraph-II (For Q. Nos. 13 and14)

Pseudohalides are anions having resemblance with halide ions. Group I metals can form salts with pseudohalides. Pseudohalogens can act as ligands and form coordinate complexes. Their hydrides are weakly acidic and can be prepared in analogous way as halogen hydrides are prepared.

13. Sodium cyanide reacts with H_2SO_4, the product formed is

(a) HCN and $NaHSO_4$

(b) $(CN)_2Na_2SO_4$ and H_2O

(c) HCN and Na_2SO_4

(d) N_3H and H_2O

14. When sodium azide reacts with conc. H_2SO_4, the product formed is
(a) ascorbic acid (b) hydrazoic acid
(c) hydrochloric acid (d) None of these

Paragraph-III (For Q. Nos. 15 and 16)

Fuel cells are galvanic cells in which chemical energy of fuel is directly converted into electrical energy. A type of fuel cell is a hydrogen-oxygen fuel cell. It consists of two electrodes made up of two porous graphite impregnated with a catalyst like Pt, Ag or metal oxide. The electrodes are placed in aqueous-solution of NaOH. Oxygen and hydrogen are continuously fed into the cell. Hydrogen gets oxidised to H^+ which is neutralised by $\overset{-}{O}H$.

At anode $H_2 \rightleftharpoons 2H^+ + 2e^-$

$$2H^+ + 2\overset{-}{O}H \rightleftharpoons 2H_2O$$

$$H_2 + 2\overset{-}{O}H \rightleftharpoons 2H_2O + 2e^-$$

At cathode O_2 gets reduced to $\overset{-}{O}H$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4\,\overset{-}{O}H$$

Overall reaction

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

The overall reaction has

$\Delta H = -285.6$ kJ mol^{-1} and $\Delta G = -237.4$ kJ mol^{-1} at 25°C

15. What is the value of $\Delta S^{\ominus}$ for the fuel cell at 25°C?
(a) 1600 JK^{-1} (b) -1600 JK^{-1} (c) 160 JK^{-1} (d) -160 JK^{-1}

16. If the concentration of hydroxide ion in the cell is doubled, then the cell-voltage will be
(a) unchanged (b) increased by a factor of 2
(c) increased by a factor of 4 (d) reduced by half

Matching Type

17. Match the following.

Column I	Column II
A. $[CO(en)_3]^{3+}$	p. Hexadentate
B. EDTA	q. Bidentate
C. en	r. Optically active
D. $[Ni(DMG)_2]^{2+}$	s. Insoluble complex

Codes

	A	B	C	D		A	B	C	D
(a)	r	p	s	q	(b)	p	r	q	s
(c)	r	p	q	s	(d)	s	p	r	q

18. Match the following.

Column I (Metal)	Column II (Extraction process)
A. Silver	p. Fused salt electrolysis
B. Calcium	q. Carbon reduction
C. Zinc	r. Carbon monoxide reduction
D. Iron	s. Amalgamation
E. Copper	t. Self reduction

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	p	q	r	t,s	s	(b)	s	p	q	q,r	t
(c)	s	p,q	q	r	t	(d)	s	t,s	r	q,r	p

19. Match the following.

Column I	Column II
A. Diffusion of a gas	p. High when molecular mass is low
B. Compressibility of a gas, $Z < 1$	q. $V_{real} < V_{ideal}$
C. v_{rms}	r. Increases with increase in temperature
D. Liquification of a gas	s. Attractive force dominates

Codes

	A	B	C	D		A	B	C	D
(a)	p	r	q	s	(b)	r	p	q	s
(c)	p	s	r	q	(d)	p	q	r	s

20. Match the following.

Column I	Column II
A. D-glucose	p. $[Cu(NH_3)_4]^{2+}(OH)_2$ + Tartarate ion
B. Sucrose	q. Mutarotation
C. Lactose	r. $[Cu(NH_3)_4]^{2+}(OH)_2$ + citrate ion
D. Maltose	s. Maltase

Codes

	A	B	C	D
(a)	p	s	r	p, r, s
(b)	q	s	p	p, r, s
(c)	p, s	q, r	r	r, s
(d)	q, r	r	q, s	q, s

Answers

Paper 1

1. (a, b, d)	**2.** (b, c, d)	**3.** (c)	**4.** (a, c)	**5.** (a,b,d)	**6.** (a,c,d)	**7.** (a,d)	**8.** (a)	**9.** (b,d)	**10.** (a,c,d)
11. (3)	**12.** (3)	**13.** (4)	**14.** (5)	**15.** (1)	**16.** (0)	**17.** (1)	**18.** (4)	**19.** (2)	**20.** (3)

Paper 2

1. (b)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (a)	**7.** (c)	**8.** (b)	**9.** (c)	**10.** (a)
11. (d)	**12.** (c)	**13.** (c)	**14.** (b)	**15.** (d)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (d)	**20.** (b)

TARGET PMT 2016

TEST Tuner 4

Comprehensive Simulator Test Series for AIPMT & AIIMS

AIPMT

Scale UP

Questions to Measure Your Problem Solving Skills

Instructions

- This test consists of 45 questions and each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

1. Four successive members of the first row of transition elements are listed below with their atomic numbers:

$${}_{23}\mathrm{V},\ {}_{24}\mathrm{Cr},\ {}_{26}\mathrm{Fe},\ \text{and}\ {}_{25}\mathrm{Mn}$$

Which one of them is expected to have the highest third ionisation enthalpy?

(a) Vanadium (b) Chromium
(c) Iron (d) Manganese

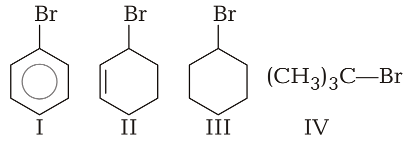
2. Number of isomeric forms for $[\mathrm{Rh(en)_2(NO_2)(SCN)}]^+$ are

(a) 3 (b) 6 (c) 9 (d) 12

3. Which one of the following is wrongly matched?

(a) $[\mathrm{Cu(NH_3)_4}]^{2+}$ - has square planar geometry
(b) $[\mathrm{Ni(CO)_4}]$ - contains neutral ligand
(c) $[\mathrm{Fe(CN)_6}]^{3+}$ - sp^3d^2 hybridised
(d) $[\mathrm{Co(en)_3}]^{3+}$ - follows EAN rule

4. The increasing order of hydrolysis for the following compounds is



(a) I < III < II < IV (b) I < II < III < II
(c) IV < II < III < I (d) I < III < IV < II

5. What is the freezing point of a solution containing 8.1 g HBr in 100 g of water, assuming the acid to be 90% ionised? ($K_f(\mathrm{H_2O}) = 1.86\ \mathrm{K\ mol^{-1}kg}$)

(a) 0.85°C (b) –3.53°C
(c) 0°C (d) –0.35°C

6. $\mathrm{Cu^+}(aq)$ is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction,

$$2\mathrm{Cu^+}(aq) \rightleftharpoons \mathrm{Cu^{2+}}(aq) + \mathrm{Cu}(s)$$

Choose the correct $E°$ for above reaction, if

$$E°_{\mathrm{Cu^{2+}/Cu}} = 0.34\,\mathrm{V};\ E°_{\mathrm{Cu^{2+}/Cu^+}} = 0.15\,\mathrm{V}$$

(a) –0.38 V (b) +0.49 V (c) +0.38 V (d) –0.19 V

7. For the second order reaction, concentration (x) of the product at time (t) starting with initial concentration $[A]_0$ is

(a) $\dfrac{kt + [A]_0^2}{1 + kt\ [A]_0^2}$ (b) $\dfrac{k + [A]_0^2}{1 + kt}$ (c) $\dfrac{1 + kt[A]_0^2}{k + [A]_0^2}$ (d) None of these

8. Which of the following statements is wrong for physisorption?

(a) It is a reversible reaction (b) Requires activation energy
(c) Adsorption enthalpy value is low
(d) Generally occurs at low temperature

9. The temperature of the slag zone in the metallurgy of the iron using blast furnace is

(a) 1500-1600°C (b) 400-700°C
(c) 800-1000°C (d) 1200-1000°C

10. Select correct statements regarding behavior of HF as non-aqueous solvent.

(a) HCl behaves as an acid and HF as a base
(b) $\mathrm{HClO_4}$ behaves as a base and HF as an acid
(c) $\mathrm{HNO_3}$ and $\mathrm{H_2SO_4}$ behave as base and HF as an acid
(d) All of the above are correct statements

11. Among the following molecules,

I. XeO_3 II. $XeOF_4$ III. XeF_6

those having same number of lone pairs on Xe are

(a) I and III
(b) I and II
(c) II and III
(d) I, II and III

12. By the electrolysis of aqueous sodium succinate, ethene is formed at .... along with ....

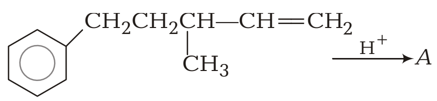
(a) anode, H_2 (b) cathode, H_2
(c) anode, CO_2 (d) cathode, CO_2

13. Identify the alkyne in the following sequence of reaction.

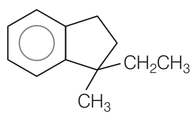
$$\text{Alkyne} \xrightarrow[\text{Lindlar's catalyst}]{H_2} A \xrightarrow{\text{Ozonolysis}} \underset{\text{only}}{B} \xleftarrow[\text{process}]{\text{Wacker}} CH_2{=}CH_2$$

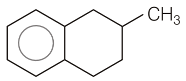
(a) $CH_3—C{\equiv}C—CH_3$
(b) $CH_3—CH_2—C{\equiv}CH$
(c) $CH_2{=}CH—C{\equiv}CH$
(d) $HC{\equiv}C—CH_2—C{\equiv}CH$

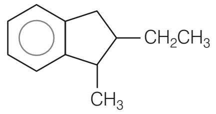
14.

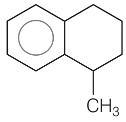


A is

(a)


(b)


(c)


(d)


15. The number of β-particles emitted during the transformation of ${}^{x}_{y}A$ to ${}^{m}_{n}B$ is

(a) $\frac{n-m}{4}$ (b) $n+\frac{x-m}{4}+y$
(c) $x+\frac{x-m}{4}+y$ (d) $2y-n+x-m$

16. 50 mL solution of $BaCl_2$ (20.8% w/V) and 100 mL solution of H_2SO_4 (9.8% w/V) are mixed, $BaSO_4$ formed is

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4(\downarrow) + 2HCl$$

(a) 23.30 g (b) 46.60 g
(c) 29.80 g (d) 11.65 g

17. Wave number of a spectral line for a given transition is x cm^{-1} for He^+, then its value for Be^{3+} (isoelectronic of He^+) for same transition is

(a) x cm^{-1} (b) 4x cm^{-1}
(c) $\frac{x}{4}$ cm^{-1} (d) 2x cm^{-1}

18. Match the Column I (Elements) with Column II (Unique properties).

	Column I		Column II
A.	F	p.	Maximum ionisation energy
B.	Cl	q.	Maximum electronegativity
C.	Fe	r.	Maximum electron affinity
D.	He	s.	Recently named by IUPAC
E.	Ds	t.	Variable valency

Codes

	A	B	C	D	E
(a)	t	q	r	s	p
(b)	p	s	t	r	q
(c)	q	r	t	p	s
(d)	s	p	r	q	t

19. Match the species in Column I with their structures in Column II.

	Column I		Column II
A.	ClF_3	p.	Square planar
B.	PCl_5	q.	Tetrahedral
C.	IF_5	r.	Trigonal bipyramidal
D.	CCl_4	s.	Square pyramidal
E.	XeF_4	t.	T-shape

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	p	r	t	s	q	(b)	t	r	s	q	p
(c)	q	s	r	t	p	(d)	r	s	t	p	q

20. Consider the following pairs of gases (A and B).

I. CO_2, N_2O II. CO, N_2
III. O_2, O_3 IV. H_2O, D_2O

Relative rates of effusion of gases A and B is in the order:

(a) I < II < III < IV (b) I = II < III < IV
(c) I = II < IV < III (d) I = II < IV < III

21. Concentrations of benzoic acid, which is distributed in two layers of water and benzene are (in three different samples)

	Water (C_1)	Benzene (C_2)
Sample I	0.3	0.09
Sample II	0.4	0.16
Sample III	0.5	0.25

Hence, benzoic acid is

(a) monomer in both layers
(b) dimer in both layers
(c) monomer in water and dimer in benzene
(d) monomer in benzene and dimer in water

22. A monoatomic ideal gas undergoes a process in which ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?

(a) $\frac{4R}{2}$ (b) $\frac{3R}{2}$
(c) $\frac{5R}{2}$ (d) 0

23. 44 g of $CH_3COOC_2H_5$ is formed at equilibrium, when 60 g of CH_3COOH and 46 g of CH_3CH_2OH react in 5 L flask. Calculate amount of $CH_3COOC_2H_5$ formed, when 120 g of CH_3COOH and 46 g of CH_3CH_2OH is taken.

(a) 58.66 g (b) 20.33 g (c) 22 g (d) 44 g

24. There is maximum pH change in case,

(a) 1 mL of a solution, pH equals to 2, is diluted to 100 mL

(b) 0.01 mole of NaOH, is added to 100 mL of 0.01M NaOH solution

(c) 100 mL of H_2O is added to 900 mL of 10^{-6}M HCl

(d) 100 mL of a solution, pH equals to 2, is mixed with 100 mL of a solution of pH equals to 12

25. Sodium crystallises in bcc arrangement with the interfacial separation between the atoms at the edge of 53 pm. The density of the solid is

(a) 1.23 g/cc (b) 485 g/cc (c) 4.85 g/cc (d) 123 g/cc

26. Which one of the following reactions involves oxidation and reduction both?

(a) $H_2 + Br_2 \longrightarrow 2HBr$

(b) $NaBr + HCl \longrightarrow NaCl + HBr$

(c) $HBr + AgNO_3 \longrightarrow AgBr + HNO_3$

(d) $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

27. Electrolysis of aqueous solution of the compounds liberates H_2 gas at both cathode and anode except in

(a) LiH (b) NaH (c) HCOONa (d) NaCl

28. Which of the following is the incorrect statement?

(a) Alkali metals form two types of sulphides : M_2S and M_2S_n (n = 2, 3, 4)

(b) Alkali metals form covalent hydrides and are non-reactive with water

(c) Alkali carbides are decomposed by H_2O forming acetylene

(d) Solubility of alkali carbonates in the order

$$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3$$

29. Amphoteric nature is shown by

(a) Be, Mg and La (b) Be, Ca and Al

(c) Be, Zn and Al (d) Ca, Mg and Sr

30. Select the correct statement(s).

(a) Aluminium dissolves in dilute mineral acids but is made passive by concentrated nitric acid

(b) Aluminium vessel can be used as storage for NaOH

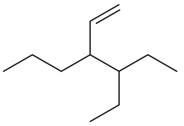
(c) Both of the above

(d) None of the above

31. The strongest Lewis acid among the boron halides is

(a) BF_3 (b) BCl_3 (c) BBr_3 (d) BI_3

32. The correct IUPAC name of the compound,



is

(a) 3-(1- ethyl propyl) hex-1-ene

(b) 4-ethyl -3-propylhex-1-ene

(c) 3-ethyl - 4 - ethenylheptane

(d) 3 - ethyl - 4 - propylhex-5-ene

33. $\underset{A}{C_6H_4Cl_2} \xrightarrow{Cl_2/Cl^+} \underset{B}{C_6H_3Cl_3}$

Which of the following statement is/are correct?

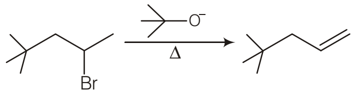
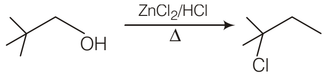
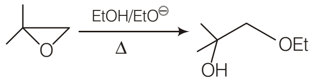
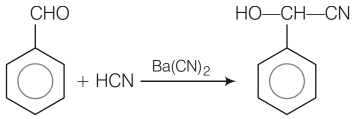
(a) *o*-isomer of *A* will give two types of *B*

(b) *m*-isomer will give three types of *B*

(c) *p*-isomer will give one type of *B*

(d) All of the above are correct statements

34. Match the Column I (Reactions) with Column II (Types of reaction).

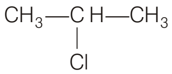
	Column I		Column II
A.		p.	Nucleophilic addition
B.		q.	E2
C.		r.	S_N2
D.		s.	S_N2
		t.	E1

Codes

	A	B	C	D		A	B	C	D
(a)	q	r	s	p	(b)	q	s	p	q
(c)	s	r	q	p	(d)	s	p	q	r

35. By which species in Wurtz reaction, only one type of hydrocarbon is obtained?

(a) CH_3CH_2Cl (b) $PhCH_2Cl$

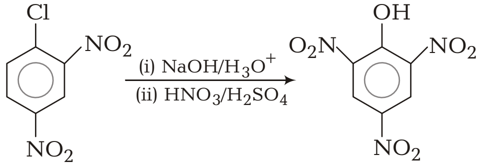
(c) 

$CH_3-\underset{\underset{Cl}{|}}{C}H-CH_3$

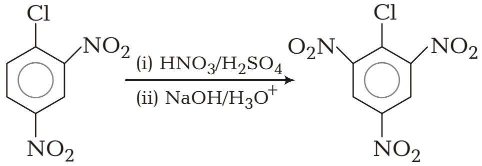
(d) All of these

36. Consider the following reactions for the formation of picric acid.

I.



II.

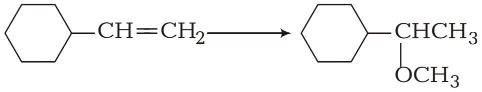


Which of the above paths is/are possible?

(a) Path I (b) Path II

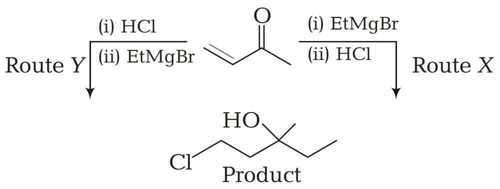
(c) Both I and II (d) None of these

37. Indicate the reagent in the following conversion:



(a) H_3O^+/CH_3OH
(b) $B_2H_6/H_2O_2, \bar{O}H/CH_3OH$
(c) $Hg(OAc)_2, CH_3OH/NaBH_4, \bar{O}H$
(d) All of the above

38. Which of the two routes shown below, actually lead to the product?



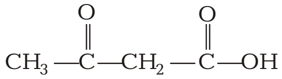
(a) Route X (b) Route Y
(c) Both (a) and (b) (d) None of these

39. Which of the following statements is incorrect?
(a) CrO_4^{2-} solution turns yellow to orange upon addition of acid
(b) $Fe^{3+}(aq)$ reacts with KSCN (aq) to give deep real solution
(c) Copper metal reacts with nitric acid to give NO gas and a blue solution
(d) A deep green solution of $Cr(OH)_3$ in excess base turns orange on addition of hydrogen peroxide

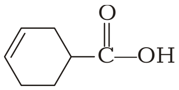
40. Consider the following carboxylic acids.

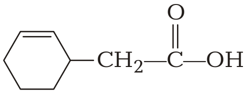
I. 

$CH_2{=}CHCH_2C({=}O){-}OH$

II. 

$CH_3{-}C({=}O){-}CH_2{-}C({=}O){-}OH$

III. 

VI. 

Indicate the compounds in which decarboxylation takes place on heating.
(a) III and IV (b) I and III
(c) II and IV (d) I and II

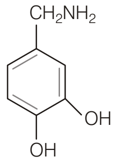
41. Which of the following statements is correct?
(a) Aniline is a stronger base than ethyl amine
(b) Aniline is a stronger base than *p*-methane aniline
(c) Aniline must be acetylated before nitration with an acid derivative
(d) Aniline is soluble in an ammonium hydroxide solution.

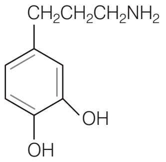
42. Commonly used catalyst in the preparation of a acrylonitrile from propylene, ammonia and order is
(a) silver (b) bismuth molybdate
(c) cerium chloride (d) nickel

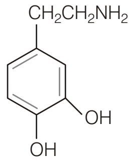
43. The one which has least iodine value is
(a) ginger oil (b) ghee
(c) groundnut oil (d) sunflower oil

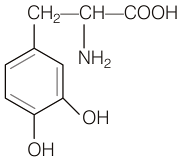
44. A polymer is made of 30% molecules of molar mass 20000; 40% molecules of molar mass 30000 and rest have 60000. Calculate the number average and weight average of molecular masses.
(a) 36000;43333
(b) 48000;5666
(c) 43333;36000
(d) 56666;48000

45. Parkinson's disease is linked to abnormalities in the levels of dopamine in the body. The structure of dopamine is

(a) 

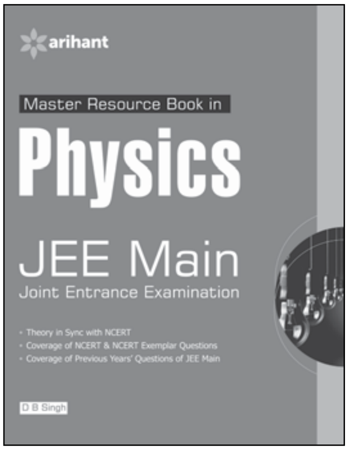
(b) 

(c) 

(d) 

Answers

1. (d)	**2.** (d)	**3.** (c)	**4.** (d)	**5.** (b)	**6.** (c)	**7.** (a)	**8.** (b)	**9.** (c)	**10.** (c)
11. (d)	**12.** (c)	**13.** (a)	**14.** (a)	**15.** (c)	**16.** (d)	**17.** (b)	**18.** (c)	**19.** (b)	**20.** (c)
21. (c)	**22.** (a)	**23.** (a)	**24.** (d)	**25.** (a)	**26.** (a)	**27.** (d)	**28.** (b)	**29.** (c)	**30.** (a)
31. (d)	**32.** (b)	**33.** (d)	**34.** (a)	**35.** (b)	**36.** (a)	**37.** (c)	**38.** (b)	**39.** (d)	**40.** (d)
41. (c)	**42.** (b)	**43.** (b)	**44.** (a)	**45.** (c)					



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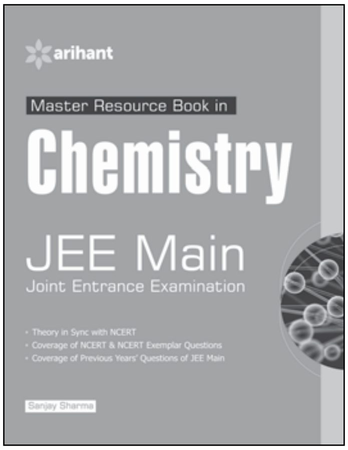

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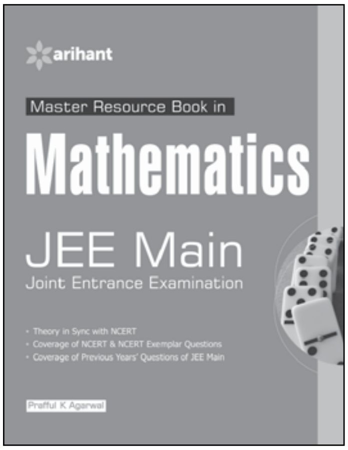

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Prafful K Agarwal

{SPECIAL PROBLEM SOLVING METHODS}

SOLUTION

CHEMISTRY CONCENTRATE

RAOULT'S LAW

The following types of problems are asked:

Type 1 If mole fraction of a volatile component (A) is given and asked to find out partial pressure of this component, use the following formula, $p_A = p_A^\circ \chi_A$

Here, p_A, p_A° and χ_A are the partial pressure, vapour pressure in pure state and mole fraction of A respectively.

Type 2 If vapour pressures and masses of all components are given and asked to find out total vapour pressure of solution, use the following steps:

- Find out mole fraction of each component

$$\chi_A = \frac{n_\mathbf{A}}{n_A + n_B + n_c + \dots}$$

$$\left(\text{Number of moles } (n) = \frac{\text{Mass (in gram)}}{\text{Molecular mass (g/mol)}}\right)$$

- Find out partial pressure of each component by using formula mentioned in Type 1.
- Find out total vapour pressure as

$$p_T = p_A + p_B + p_C + \dots\dots$$

Type 3 If vapour pressure of solution is given at different conditions and asked to find out vapour pressure in pure state, form two different equations for two different cases with the help of Raoult's law, solve these equations and find out vapour pressure of solution in pure state.

Solve the Following Problems

1. The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.
2. Two liquids *A* and *B* form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of *A* and 3 moles of *B* is 550 mm of Hg. At the same temperature, if one more mole of *B* is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressures of *A* and *B* in their pure states.

CHEMISTRY CONCENTRATE

COLLIGATIVE PROPERTIES

The following types of problems are asked:

Type 1 When K_b and molality of solution (m) are given and asked to find out elevation in boiling point, (ΔT_b) apply the following formula, $\Delta T_b = K_b \times m$

Type 2 When T_b, enthalpy of vaporisation ($\Delta_{vap}H$) and molecular mass of solvent are given and asked to find out K_b, apply the following formula,

$$K_b = \frac{M_{\text{solvent}} \cdot RT_b^2}{1000 \times \Delta_{\text{vap}}H} = \frac{RT_b{}^2}{1000\, l_v}$$

l_v = latent heat of vaporisation.

Type 3 When K_b and molality (m) are given and asked to find the temperature at which solution boils apply the following formula, $T = T_b + K_b m$

Type 4 When ΔT_b and K_b are given and asked to find out mole fraction, apply the following formula,

$$\frac{\Delta T_b}{K_b} = \frac{\chi_{\text{solute}} \times 1000}{M_{\text{solvent}} \times \chi_{\text{solvent}}}$$

Type 5 When weight of solute, volume of solution and temperature are given and asked to find out osmotic pressure, use the following formula,

$$\pi = \frac{W_{\text{solute}} \times RT}{M_{\text{solute}} \times V_{\text{solution}}} = \frac{n_{\text{solute}} \times RT}{V_{\text{solution}}}$$

If density of solution is asked, use the following formula, $d = \dfrac{\pi M_{\textbf{solute}}}{RT}$

Type 6 When osmotic pressures of different solutions are given and asked to find out osmotic pressure of their mixture, use the following formula,

$$\pi_{\text{(total)}} = \pi_1 + \pi_2 + \pi_3 + \dots\ .$$

$$= \frac{n_1RT}{(V_1 + V_2 + \dots.)} + \left(\frac{n_2RT}{V_1 + V_2 + \dots.}\right) + \dots.$$

Type 7 When weights of solute and solvent are given and asked to find out relative lowering in vapour pressure, use the following formula

$$\frac{p^\circ - p^s}{p^\circ} \approx \frac{n}{N} \approx \frac{w_{\text{solute}} \times M_{\text{solvent}}}{w_{\text{solvent}} \times M_{\text{solute}}}$$

Note For problems related to depression in freezing points consider first four types and use ΔT_f, K_f, ΔH_{fusion} and l_{fusion} in place of ΔT_b, K_b, ΔH_{vap} and l_v.

Solve the Following Problems

3. Vapour pressure of an aqueous solution of glucose at 373 K is 750 mm of Hg. Calculate the molality of solution.
4. When 6 g of glucose was added in 50 g of water, 0.34°C elevation in boiling point was recorded. Calculate the molal elevation constant of water.
5. The boiling point of a solution containing 1g of substance dissolved in 83.4 g of benzene is 80.175°C. If latent heat of vaporisation and boiling point of benzene are 90 cal/g and 80°C respectively. Calculate the molar mass of solute.

CHEMISTRY CONCENTRATE

ABNORMAL COLLIGATIVE PROPERTIES

For solving problems related to abnormal colligative properties you may go through following steps:

Step 1 Calculate van't Hoff factor (i)

$$(i) = \frac{\text{Calculated molar mass } (M_c)}{\text{Observed molar mass } (M_o)}$$

Step 2 If one molecule dissociates into n ions, degree of dissociation is given as

$$\alpha = \frac{i-1}{n-1}$$

If n molecules associate to form a gaint molecule, degree of association is given as

$$\alpha = \frac{i-1}{\frac{1}{n}-1}$$

Step 3 For calculation of colligative properties, use following modefied expressions,

(i) Relative lowering in vapour pressure,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = i\chi_B$$

(ii) $\Delta T_f = iK_f m$

(iii) $\Delta T_b = iK_b m$

(iv) $\pi = i\frac{n}{V}RT$

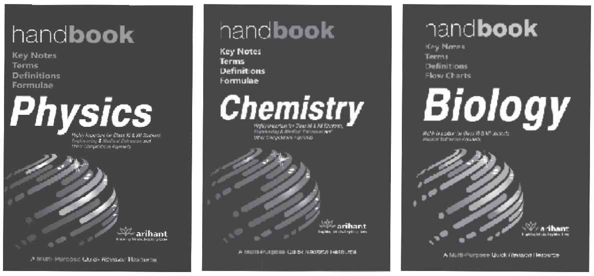
Solve the Following Problem

6. Predict the correct order of osmotic pressure of the following solutions.

(a) 0.1 N NaCl

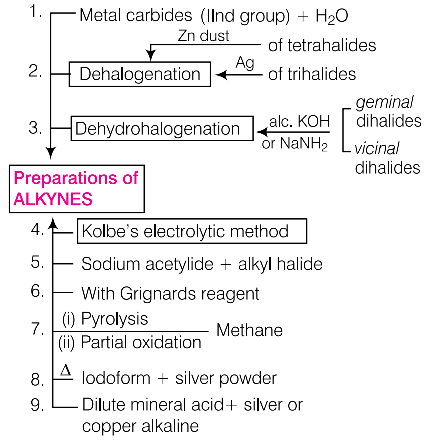
(b) 0.1N Na_2SO_4

(c) 0.1N Na_3PO_4

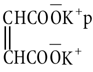


ALKYNES (C_nH_{2n-2})

These form the second series of unsaturated hydrocarbons with higher possible degree of unsaturation. These contain two π-bonds and one σ-bond between two carbon atoms. This group of three bonds is often called **acetylenic bond.**



Reaction 4 Electrolysis of potassium fumerate



$\begin{array}{l}\text{CHCO}\bar{\text{O}}\text{K}^{+}\\ \|\\ \text{CHCO}\bar{\text{O}}\text{K}^{+}\end{array}$ produces acetylene with the liberation of CO_2 and H_2 at anode and cathode respectively.

Reaction 5 This reaction is used to prepare higher alkynes.

Reaction 6 Grignard reagent helps to prepare higher alkynes from lower alkynes.

Reaction 7 (i) Pyrolysis of methane takes place in a flow system with short contact time.

$$2CH_4 \xrightarrow[0.01-0.10\text{ s}]{1500^\circ C} CH \equiv CH + 3H_2$$

(ii) Partial oxidation of methane in controlled high temperature gives ethyne.

$$6CH_4 + O_2 \longrightarrow 2CH \equiv CH + 2CO + 4H_2$$

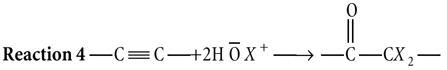
Reaction 9 $M-C \equiv C-M + 2HCl \longrightarrow 2MCl\downarrow + CH \equiv CH; M = Ag, Cu$

Physical Properties of Alkynes

- First three members are colourless gases, next eight are liquids and higher alkynes are solids.
- All alkynes are colourless and odourless except acetylene (garlic odour).
- Melting point, boiling point and densities of alkynes are higher than the corresponding alkenes and alkanes.
- Acetylene and terminal alkynes are acidic in nature.
- Order of acidity for different alkynes is, $HC \equiv CH > CH_3-C \equiv CH >> CH_3-C \equiv C-CH_3$

Reaction 2 Liquid bromine yields tetrabromo derivative while bromine water or Br_2/CCl_4 forms dibromo derivative.

Reaction 3 $-C \equiv C- + 2HX \longrightarrow \underset{(gem\text{ dihalide})}{-CH_2-CX_2-}$



Reaction 4 $-C \equiv C- + 2H\bar{O}X^{+} \longrightarrow -\overset{\overset{O}{\|}}{C}-CX_2-$

Reaction 5 Hydration occurs in the presence of 1% $HgSO_4$ and 42% H_2SO_4.

Reaction 6 Acetylene gives vinyl cyanide on the polymerisation by which synthetic fibre orlon (acrylonitrile) is obtained.

Reaction 7 The reaction with Na in liq. NH_3 is considered as the test of acidity.

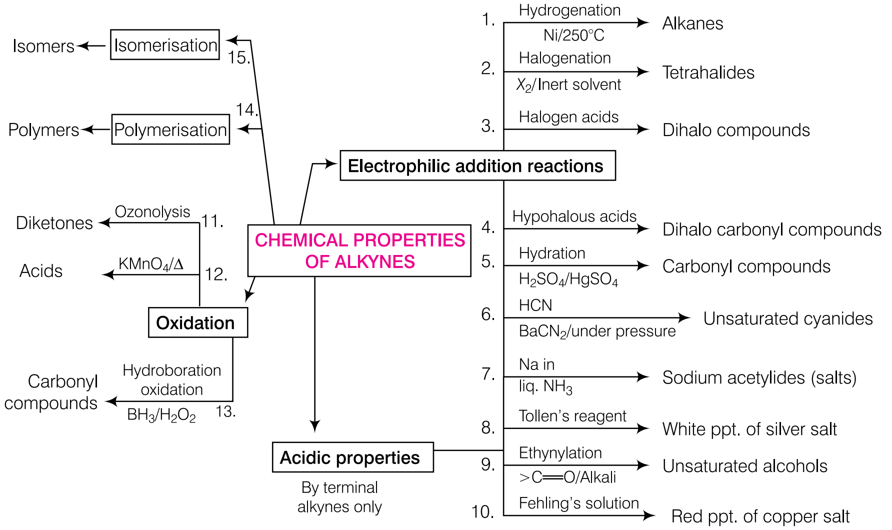
Reaction 8 With Tollen's reagent (ammonical $AgNO_3$), a white precipitate of silver salt is obtained. This reaction is used to differentiate between terminal (acidic) alkynes with rest of the alkynes i.e. helpful in detecting the position of triple bond (interstitial or terminal).

Reaction 9 Terminal alkynes work as nucleophile, thus add to $-C=O$ group through nucleophilic addition in the presence of base.

Reaction 10 Fehling's solution is also used for the same purpose as that Tollen's reagent is used. Terminal alkynes with Tollen' reagent give red precipitate of their copper salt.

Reaction 14 When vapours of alkynes are passed through red hot Cu or Fe tube, aromatic compounds are produced.

Reaction 15 On heating with alc. KOH or $NaNH_2$ in inert solvent, the triple bond of 1-alkyne is shifted towards the centre to form an isomeric 2-alkyne. On heating with sodamine ($NaNH_2$ in liquid NH_3), the triple bond shift towards the end.



- $R-C \equiv C-R$ with hot $KMnO_4$ produces carboxylic acids ($RCOOH$)
- $CH \equiv CH$ with hot $KMnO_4$ gives oxalic acid while rest of acidic alkynes ($R-C \equiv CH$) produces CO_2 alongwith acid ($RCOOH$)

Ozonolysis of alkynes give different products in different media such as dicarbonyl in Zn/CH_3COOH, acids or ketones in H_2O_2 and glycol in $LiAlH_4$.

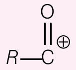
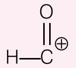
Contrary to hydration, in case of hydroboration oxidation, alkynes give aldehydes.

Revisi
CONCE
HYDROCARB

ELECTROPHILIC SUBSTITUTION REACTION IN BENZENE

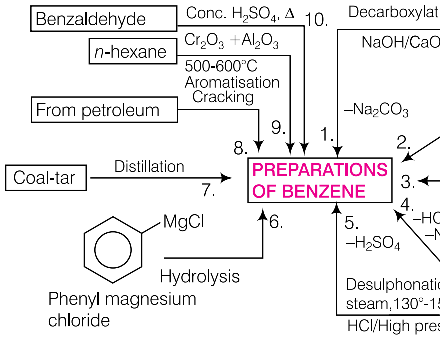
- Benzene undergoes electrophilic substitution reactions, e.g. halogenation, nitration, sulphonation, Friedel-Crafts reaction etc.
- This substitution proceeds through following three steps:

***Step* 1 Formation of electrophile** (E^+) The electrophiles formed in different electrophilic substitution reactions are:

Electrophile	Reaction name
Cl^+	Halogenation
NO_2^+	Nitration
SO_3	Sulphonation
R^+	Friedel-Crafts alkylation
 $R-\overset{\overset{O}{\|}}{C}^{\oplus}$	Friedel-Crafts acylation
 $H-\overset{\overset{O}{\|}}{C}^{\oplus}$	Formylation
$H-\overset{\oplus}{C}=NH$	Gattermann synthesis

AROMATIC HYDROCARBONS

- The main source of these is coal.



Reaction 4 Benzene diazonium chloride is reduced to benzene by $SnCl_2$ and NaOH or absolute ethyl alcohol or hypophosphorous acid (H_3PO_2).

Reaction 7 The distillation of coal-tar gives following fractions:

(i) **Light oil** Below 200°C, contains BTX (Benzene, Toluene and Xylene) as its chief components.

(ii) **Middle oil** 200-240°C, contains phenols, cresols and naphthalene.

(iii) **Heavy oil** 245-280°C contains cresols and naphthalene.

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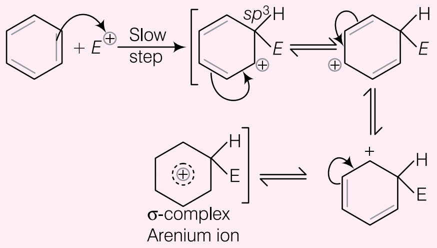
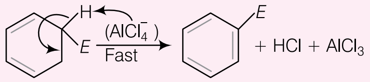
PT MAP
ONS (PART II)

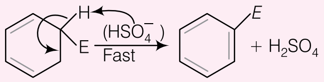
***Step* 2 Formation of carbocation intermediate**



***Step* 3 Loss of a proton from the carbocation intermediate**

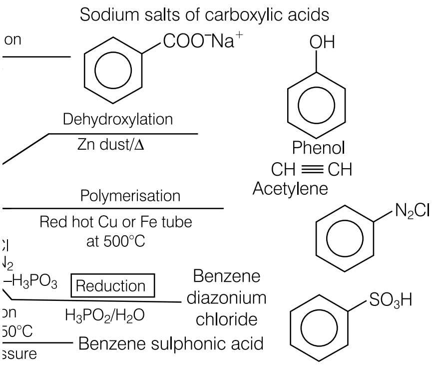


In case of chlorination, Friedel-Crafts reaction Gattermann's reaction.



(In case of nitration and sulphonation)

Note ***Step*** 3 is fast step, hence, it does not affect the rate of reaction.



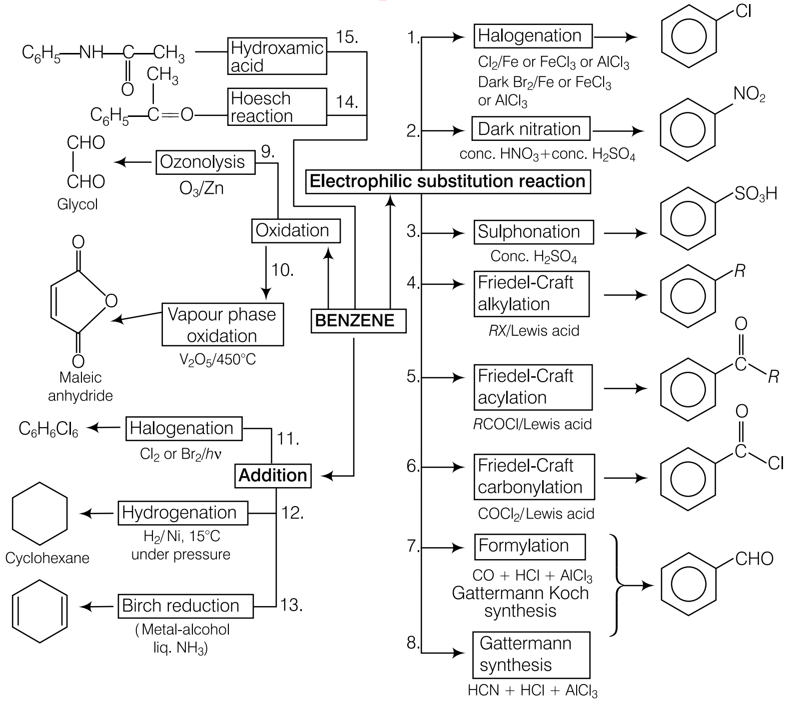
(iv) **Anthracene oil** 280-405°C contains anthracene, phenanthrene and carbazole.

(v) **Pitch** The residue containing 5 and 6 membered fused rings and tar oils.

Physical properties of benzene

- Benzene is a colourless liquid.
- Melting point −5.5° C, boiling point −80.1° C insoluble in water, miscible with alcohol, ether and chloroform.
- A good solvent, highly toxic vapours, burns with a luminous sooty flame.

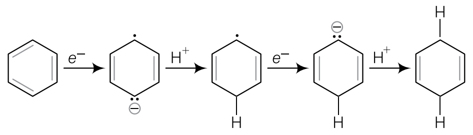
Chemical Properties of BENZENE



Reaction 1 Benzene undergoes chlorination when it is treated with chlorine in presence of catalyst aluminium chloride or ferric chloride and in absence of light.

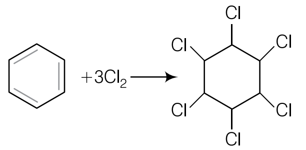
Reaction 10 In this reaction, first maleic acid $\begin{array}{c}\text{CHCOOH}\\ \|\\ \text{CHCOOH}\end{array}$ is produced which loses water at 450° C and converted into anhydride.

Reaction 11, 12 and 13 Reaction 11 and 12 operate through free radical mechanisms while in reaction 13 the metal used is of Ist group i.e., Li, Na (mostly Na) and alcohol normally CH_3OH ((or C_2H_5OH). Here, metal works for electron donation and alcohol for proton donation as : $Na \longrightarrow Na^+ + \bar{e}$

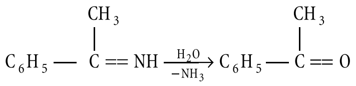


- Here, proton is provided by alcohol.
- At high temperature, alcohol is not needed, H^+ is provided by NH_3 and product obtained is cyclohexene.

Note The uniqueness of pathway here is that the addition is throughout 1, 4-addition, i.e. initially cyclohexa-1,4-diene is formed which on further 1,4 -addition gave cyclohexene. The product of reaction 11 is $C_6H_6Cl_6$. It is also called lindane or gammexane or 666 and is used as insecticide.

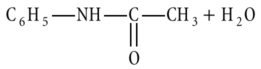


Reaction 14 $C_6H_6 + CH_3—CN \xrightarrow[ZnCl_2]{HCl} C_6H_5$



$$C_6H_5—\overset{\overset{\displaystyle CH_3}{|}}{C}{=\!=}NH \xrightarrow[-NH_3]{H_2O} C_6H_5—\overset{\overset{\displaystyle CH_3}{|}}{C}{=\!=}O$$

Reaction 15 $C_6H_6 + CH_3CONHOH \xrightarrow[\text{acid, } \Delta]{\text{Polyphosphoric}}$



$$C_6H_5—NH—\underset{\underset{\displaystyle O}{\|}}{C}—CH_3 + H_2O$$

DIRECTIVE INFLUENCE OF FUNCTIONAL GROUPS

- When a functional group is attached to benzene ring and subjected to electrophilic substitution reactions, electron releasing functional groups like —OH, $—NH_2$, —*OR* etc., direct the incoming electrophile, towards *ortho* and *para*-positions and itself acts as an activating group, while an electron withdrawing functional group like $—NO_2$, —COOH, —CHO etc., direct the incoming electrophile, towards *meta*-position.
- —F, —Cl, —Br and —I are weakly deactivating, these are *o* and *p*-directing.

Order of activating power for different groups are as follows:

ortho/para- directing

$$\underbrace{—NH_2, —NHR, —NR_2, —OH, —OR,}_{\text{Strongly activating}} >$$

$$\underbrace{—NH\overset{\overset{\displaystyle O}{\|}}{C}R, —O\overset{\overset{\displaystyle O}{\|}}{C}R,}_{\text{Moderately activating}}\underbrace{—R, —Ar, —CH{=\!=}CR_2}_{\text{Weakly activating}},$$

$$> \underbrace{—F, —Cl, —Br}_{\text{Weakly Deactivating}}$$

***Meta*-directing**

$$\underbrace{—I > —\overset{\overset{\displaystyle O}{\|}}{C}H > —\overset{\overset{\displaystyle O}{\|}}{C}R > —\overset{\overset{\displaystyle O}{\|}}{C}OR —\overset{\overset{\displaystyle O}{\|}}{C}OH > —\overset{\overset{\displaystyle O}{\|}}{C}Cl >}_{\text{Moderate deactivating}}$$

$$\underbrace{—C{\equiv}N > —SO_3H > —\overset{+}{N}H_3 > —\overset{+}{N}H_2R > —\overset{+}{N}HR_2}_{\text{Strongly deactivating}}$$

$$> \underbrace{—\overset{+}{N}R_3 > —\overset{+}{N}O_2}_{\text{Most deactivating}}$$

JEE Final Touch

Fast Track Revision

Electrochemistry

ELECTROLYSIS, CONDUCTANCE AND CONDUCTIVITY OF ELECTROLYTIC SOLUTION

Electrochemistry is the branch of science which deals with the interaction of electrical energy with chemical species.

Electrolysis

The process of decomposition of an electrolyte (conduct electricity through ions in solutions) on passing electric current through its aqueous solution or in the fused state is called electrolysis. In electrolysis, electric current is used to bring a non-spontaneous chemical reaction (the reaction for which $G = +ve$ and $E = \quad ve$), e.g. electrolysis of molten NaCl.

$$\text{NaCl (molten)} \ ¾ \ Na^+ + Cl$$

At anode $2Cl \quad 2e \ ¾ \ Cl_2$

At cathode $2Na^+ + 2e \ ¾ \ 2Na(l)$

Faraday's Laws of Electrolysis

The laws which are governed during the decomposition of substances at electrodes with passage of electric current are called Faraday's laws of electrolysis.

Faraday's first law	Faraday's second law
The weight (w) of an ion discharged during electrolysis is directly proportional to the quantity of electricity (I) passed.	When same quantity of electricity is passed through different solution of electrolytes, the masses of different ions (say w_1 and w_2) liberated at electrodes are directly proportional to their equivalent masses (E_1 and E_2).

Preferential Discharge During Electrolysis

During electrolysis, if more than two electrolytes are present in the solution, only the ions requiring least energy are discharged in preference to other. The increasing power of deposition of some ions are given below:

For cations

$$K^+ < Na^+ < Ca^{2+} < Mg^{2+} < Al^{3+} < Zn^{2+} < H^+ < Cu^{2+} < Hg^{2+} < Ag^+$$

For anions $SO_4^2 \quad < NO_3 \quad < \overset{\ominus}{O}H < Cl \quad < Br \quad < I$

CHEMISTRY CONCENTRATE

FORMULAE FOR FARADAY'S LAW

- $w = ZIt$; Z = Electrochemical equivalent (ECE) of the ion deposited at electrode.
- $\frac{w_1}{w_2} = \frac{E_1}{E_2}$
- $E = FZ$; F = Faraday constant, 96500 C,

$$w = \frac{EIt}{96500}$$

- $w = VQ = VIt$; w = electrical energy, V = voltage, Q = charge.
- For gaseous products,

$$V_g = \frac{V_E It}{96500}$$

where, V_g = volume of gas evolved at electrode

V_E = equivalent volume of gas

For O_2, $V_E = 5.6$ L at STP

For H_2, $V_E = 11.2$ L at STP

For Cl_2, $V_E = 11.2$ L at STP

Applications of Electrolysis

- Non-metals like H_2, O_2, Cl_2 etc., are obtained by electrolysis in pure form. Alkanes are obtained by Kolbe's electrolytic method.
- Metals like Na, Al, Ca, Mg, K are obtained by the electrolysis of fused electrolytes.
- Metals like Au, Ag, Al, Sn etc., are refined by electrolysis. Inferior metals are coated with a superior metal like Ag, Au, Pt by electrolysis.
- Thickness of the coated layer can be calculated as

$$(\text{length} \times \text{breadth} \times \text{height}) \times \quad = \frac{EIt}{96500}$$

{JEE FINAL TOUCH}

Conductance and Conductivity of Electrolytic Solution

Conductance (C) is the power of an electrolytic solution to conduct electricity and is related to resistance (R) as $C = \frac{1}{R} = \frac{A}{l}$

where, is the specific resistance and is defined as the resistance of a conductor of 1 cm length and $1\,\text{cm}^2$ area of cross-section.

$\frac{l}{A}$ is called **cell constant** and has unit cm^{1}.

Units of conductance ohm^{1} or mho $({}^{1})$ or Siemen (in SI)

Types of Conductivity

There are three types of conductivity as shown in the table below:

Conductivity type	Definition	Formula	Units
Specific conductivity ( )	It is the reciprocal of specific resistance æ ç $= \frac{1}{}$ö ÷	$= \frac{1}{} = \frac{1}{R} \frac{l}{A}$ $= C$ æ ç $\frac{l}{A}$ ö ÷	${}^{1}\,\text{cm}^{1}$, S cm^{1}
Molar conductivity ($_m$ or)	It is the conducting power of a solution containing 1 g-mol of an electrolyte.	$= \frac{1000}{M} = V_{mL}$ (V_{mL} = volume of solution containing 1 g-mol of an electrolyte)	${}^{1}\,\text{cm}^2\,\text{mol}^{1}$, $\text{S m}^2\,\text{mol}^{1}$
Equivalent conductivity ($_{eq}$ or)	It is the conducting power of a solution containing 1 g-equivalent of an electrolyte	$= \frac{1000}{N} = V_{mL}$ (V_{mL} = volume of solution containing 1 g-eq of an electrolyte)	${}^{1}\,\text{cm}^2\,\text{eq}^{1}$, $\text{S m}^2\,\text{eq}^{1}$

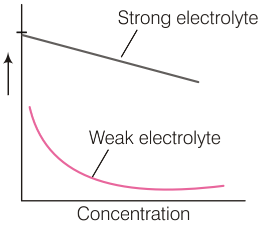
Variation of Conductivity with Dilution

- At infinite dilution, the conductivity of both weak and strong electrolytes become almost same and a weak electrolyte behaves as a strong electrolyte.
- The equivalent and molar conductivity of a solution increases with dilution, whereas the specific conductivity decreases with dilution, as the number of ions per unit volume decreases.
- The equivalent and molar conductances increase with dilution, because these are the product of specific conductance and volume of solution containing 1 equivalent and 1 mole of electrolyte respectively.

The variation of molar conductance ( ) for strong electrolyte with concentration (C) is given by **Debye-Huckel-Onsager equation** which is, $= \quad b\sqrt{C}$

where, b = constant, = molar conductance at infinite dilution

- The value of b for a given solvent and temperature depends upon the nature of electrolyte (charge on cation and anion produced after dissociation). All electrolytes of a particular type have same value of b.
- It is clear from the graph that for a strong electrolyte, extrapolation of curve at $C = 0$ gives for strong electrolytes. However, such an extrapolation cannot be made for weak electrolytes.



- The limiting value of molar conductivity for either strong or weak electrolytes can be obtained by extrapolating the respective curves to $C=0$. This limiting value of molar conductivity is known as **molar conductivity** at infinite dilution ( ).

Þ $=$ (when, C 0)

Kohlrausch's Law of Independent Migration of Ions

According to this law, "the molar conductivity at infinite dilution $_m$ of the electrolyte must be equal to the sum of the molar conductivities of the ions produced by the electrolyte at infinite dilution."

$$_{m\,(AB)} = {}_{A^+} + {}_{B^-}$$

where, $_{A^+}$ and $_{B^-}$ are the ionic /molar conductivities of cation, A^+ and anion, B^- respectively.

Applications of Kohlrausch's Law

(i) With the help of this law, we can determine the molar conductivity of weak electrolytes at infinite dilution.

(ii) For calculating degree of dissociation ( ) of weak electrolyte the formula used is $= \frac{^{C}}{}$

where, ^{C} = molar conductance at any concentration
= molar conductance at infinite dilution.

(iii) To determine the ionisation constant of a weak electrolyte.

(iv) For calculating the solubility of a sparingly soluble salt with the help of the following formula.

$$^{\circ}_{eq} = \frac{1000}{S}$$

Transport Number

- It is defined as the fraction of the current carried by an ion.
- Transport number $= \frac{\text{Current carried by an ion}}{\text{Total current carried}}$
- Transport number of cation + transport number of anion = 1.

Effect of Temperature on Conductivity

The conductance of an electrolytic solution increases with increase in temperature, because the kinetic energy of ions increases resulting to increase in the movement of ions.

For a small increase in temperature, the temperature dependence of molar conductivity is given by

$$_t = {}_{25}\,[1 + (t \quad 2b)]$$

where, = constant,
$_t$ = molar conductivity at t°C
$_{25}$ = molar conductivity at 25°C.

Molar conductivity of a dilute solution increases by around 2% per degree increase in temperature.

Best Practice SHOTS

1. Which of the following solutions has highest equivalent conductance?

(a) 0.01 M KCl (b) 0.05 M KCl
(c) 0.02 M KCl (d) 0.005 M KCl

2. If conductivity of 0.00241 M acetic acid solution is $7.896 \quad 10^{5}$ Scm^{1}, calculate its molar conductivity in this solution. If $_{m}$ for acetic acid be 390.5 Scm^2 mol^{1}, then dissociation constant is

(a) 12.2 S cm^2 mol^{1}, $1.11 \quad 10^{4}$
(b) 10.7 S cm^2 mol^{1}, $2.85 \quad 10^{4}$
(c) 22.7 S cm^2 mol^{1}, $1.85 \quad 10^{5}$
(d) 32.76 S cm^2 mol^{1}, $1.85 \quad 10^{5}$

Hint $^{C}_{m} = \frac{1000}{M}, \quad = \frac{^{C}_{m}}{_{m}}, \quad = \frac{C \quad ^2}{1}$

3. A current of 2.0 A passed for 5 h through a molten metal salt deposits 22.2 g of metal (atomic weight = 177). The oxidation state of the metal in the metal salt is

(a) +1 (b) +2 (c) +3 (d) +4

Hint $Q = It$, Oxidation state $= \frac{\text{Atomic weight}}{\text{Equivalent weight}}$

4. Ionic mobility of Ag$^+$ is ($_{Ag^+} = 5 \quad 10^{4}$ ohm^{1}cm^{2}eq^{1})

(a) $5.2 \quad 10^{9}$ (b) $2.4 \quad 10^{9}$ (c) $1.52 \quad 10^{9}$ (d) $8.25 \quad 10^{9}$

Hint Ionic mobility $= \frac{\text{Ionic conductance}}{96500}$

5. What current is to be passed for 0.25s for decomposition of a certain weight of metal which is equal to its electrochemical equivalent?

(a) 4 A (b) 100 A (c) 200 A (d) 2 A

Hint Electrochemical equivalent is the weight deposited by 1C of charge.

6. Electrolytic conduction differs from metallic conduction. In the case of electrolyte conduction

(a) The resistance increases with increasing temperature
(b) The resistance decreases with increasing temperature
(c) The flow of current does not generate heat
(d) The resistance is independent of the length of the conductor

Hint On increasing temperature the ions in the solution move faster and hence, the resistance decreases.

7. How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 m A?

(a) $2.616 \quad 10^{19}$ molecules (b) $1.216 \quad 10^{12}$ molecules
(c) $5.616 \quad 10^{19}$ molecules (d) $6.616 \quad 10^{12}$ molecules

Hint 2Cl ¾ $Cl_2 + 2e$
2 F or 2 96500 C deposit $Cl_2 = 1$ mol

8. Which of the following expressions correctly represents the equivalent conductance of $Al_2(SO_4)_3$ at infinite dilution. Given that $^{\circ}_{Al^{3+}}$ and $^{\circ}_{SO_4^{2}}$ are the equivalent conductances at infinite dilution of respective ions?

(a) $2 \ ^{\circ}_{Al^{3+}} + 3 \ ^{\circ}_{SO_4^{2}}$ (b) $^{\circ}_{Al^{3+}} + \ ^{\circ}_{SO_4^{2}}$
(c) $(\ ^{\circ}_{Al^{3+}} + \ ^{\circ}_{SO_4^{2}}) \quad 6$ (d) $\frac{1}{3} \ ^{\circ}_{Al^{3+}} + \frac{1}{2} \ ^{\circ}_{SO_4^{2}}$

9. The molar conductances of NaOH, NaCl and $BaCl_2$ at infinite dilution are $2.481 \quad 10^{2}$, $1.265 \quad 10^{2}$ and $2.800 \quad 10^{2}$ Sm^{2}mol^{1} respectively. Calculate the $^{\circ}_{m}$ for $Ba(OH)_2$.

(a) $4.232 \quad 10^{2}$ Sm^{2}mol^{1}
(b) $1.121 \quad 10^{2}$ Sm^{2}mol^{1}
(c) $5.232 \quad 10^{2}$ Sm^{2}mol^{1}
(d) $4.132 \quad 10^{2}$ Sm^{2}mol^{1}

10. The sequence of ionic mobility in the aqueous solution is

(a) $K^+ > Na^+ > Rb^+ > Cs^+$ (b) $Cs^+ > Rb^+ > K^+ > Na^+$
(c) $Rb^+ > K^+ > Cs^+ > Na^+$ (d) $Na^+ > K^+ > Rb^+ > Cs^+$

Hint Smaller the size of cation, more strongly it is hydrated and less is the ionic mobility. The sizes of the unhydrated ions increase in the order: $Na^+ < K^+ < Rb^+ < Cs^+$

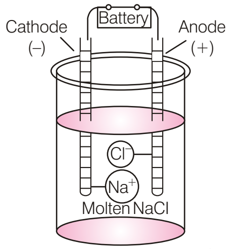
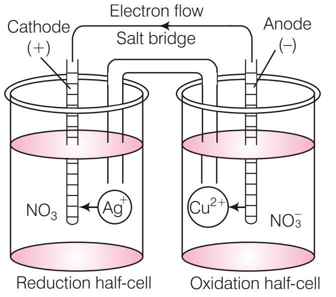
So, ionic mobility is $Cs^+ > Rb^+ > K^+ > Na^+$

ELECTROCHEMICAL CELLS, ELECTRODE POTENTIAL AND EMF OF A GAL VANIC CELL

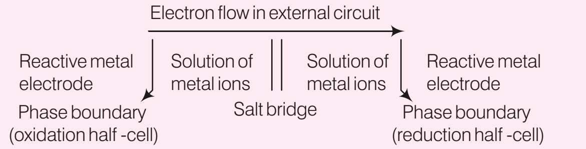
Electrochemical Cells

These are the devices in which interconversion of electrical energy and chemical energy takes place.

Types of electrochemical cells

Electrolytic cell	**Galvanic cell** (Voltaic cell)
Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
Non-spontaneous redox reaction occurs.	Spontaneous redox reaction takes place.
Anode is positive electrode and cathode is negative electrode.	Anode is negative electrode and cathode is positive electrode.
Ions are discharged at both the electrodes.	Ions are discharged only on the cathode.
If the electrodes are inert, concentration of the electrolyte decreases when the electriic current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
Both electrodes are dipped into same electrolytic solution.	Electrode reactions occur in separate half-cells.
No salt bridge needed.	Salt bridge is an essential requirement.
Working of an electrolytic cell can be shown as  Electrolysis of molten NaCl $Na^+ + Cl$ ¾ $Na(s) + \frac{1}{2}Cl_2(g)$	Working of a galvanic cell can be shown as  $2Ag^+(aq) + Cu(s)$ ¾ $Cu^{2+}(aq) + 2Ag(s)$

Representation of an Electrochemical Cell



Electrode Potential (E)

When a metal is placed in a solution of its ions, a definite potential difference is developed between the metal and the solution. This potential is called electrode potential.

Oxidation Potential

The tendency of an electrode to lose electrons or to get oxidised is called its oxidation potential.

e.g. $M(s) \rightleftharpoons M^{n+}(aq) + ne$

Such an electrode is negatively charged with respect to its salt solution.

Reduction Potential

The tendency of an electrode to gain electrons, i.e. to get reduced is known as reduction potential.

e.g. $M^{n+}(aq) + ne \rightleftharpoons M(s)$

Such an electrode is positively charged with respect to its salt solution.

Thus, $E_{\text{oxidation}} = E_{\text{reduction}}$

The electrode potential depends upon:

(i) nature of metal and its ions
(ii) concentration of ions in the solution
(iii) temperature

Standard Electrode Potential ($E°$)

The potential difference developed between metal electrodes and the solution of its ions of unit molarity at 1 atm pressure and 25°C temperature is called standard electrode potential.

If a reaction is reversed,then the magnitude of standard electrode potential remains same but the sign changes,

e.g. $E°_{\text{oxidation}} = -E°_{\text{reduction}}$

Bipotential Electrode Sensors

- Electrocardiography (ECG), electromyography (EMG) and electroencephalography (EEG) systems measure heart, muscle and brain activity respectively over time by measuring electric potentials on the surface of living tissue.
- Nervous stimuli and muscle contractions can be detected by measuring the ionic current flow in the body. This is accomplished using a **biopotential electrode.**
- The current flow in the human body is due to ion flow, not electrons.
- A biopotential electrode is a transducer that senses ion distribution on the surface of tissue and converts the ion current to electron current.

Different Types of Reference Electrodes

Some important reference electrodes are as follows:

Normal Hydrogen Electrode (NHE)

Hydrogen electrode is the primary reference electrode and it is used normally to know the electrode potential of a half-cell of galvanic cell. The reason for such a usage is that it can act as a cathode as well as an anode with respect to other electrode, due to the following reactions.

$H_2(g)$ ¾ $2H^+ + 2e$;

$2H^+ + 2e$ ¾ $H_2(g)$

The electrode potential of NHE is taken as zero. It is represented as $Pt|\ H_2(atm)\ |H^+(1M)$.

Standard Hydrogen Electrode (SHE)

A hydrogen electrode in which the pressure of H_2 gas is maintained at 1 atm and concentration of H^+ ions in the solution is 1M, is called standard hydrogen electrode (SHE).

The electrode potential for SHE is taken as 0.00 V at all temperatures.

Electrochemical Series

It is a series of chemical elements arranged in the order of their standard electrode potentials.

The standard reduction potentials of different ions with reference to SHE are given below:

Standard Electrode Potentials at 25°C "The Electrochemical Series"

Element	Electrode reaction (reduction)	Standard electrode reduction potential *E*° (volt)
Li	$Li^{+} + e$ – Li	3.05
K	$K^{+} + e$ – K	2.93
Na	$Na^{+} + e$ – Na	2.71
Mg	$Mg^{2+} + 2e$ – Mg	2.37
Al	$Al^{3+} + 3e$ – Al	1.66
Zn	$Zn^{2+} + 2e$ – Zn	0.762
Fe	$Fe^{2+} + 2e$ – Fe	0.44
Ni	$Ni^{2+} + 2e$ – Ni	0.25
Sn	$Sn^{2+} + 2e$ – Sn	0.14
H_2	$2H^{+} + 2e$ – H_2	0.00
Cu	$Cu^{2+} + 2e$ – Cu	+0.337
Ag	$Ag^{+} + e$ – Ag	+0.799
Hg	$Hg^{2+} + 2e$ – Hg	+0.885
Br_2	$Br_2^{+} + 2e$ – $2Br$	+1.08
Cl_2	$Cl_2^{+} + 2e$ – $2Cl$	+1.36
Au	$Au^{3+} + 3e$ – Au	+1.50
F_2	$F_2^{+} + 2e$ – $2F$	+2.87

Increasing tendency for reduction ↓
Increasing tendency to accept e^{-} ↓
Increasing strength as oxidising agent ↓
Increasing strength as reducing agent ↑
Increasing tendency to lose electrons ↑
Increasing tendency for oxidation ↑

Characteristics of Electrochemical Series

(i) Electrodes with negative standard reduction potential (SRP), when joined to SHE, behave as anode. Electrodes with positive SRP behave as cathode when joined to SHE.

(ii) Elements which are better reducing agents than hydrogen are placed above hydrogen (they have negative value of SRP). Elements which are better oxidising agents than hydrogen are placed below hydrogen (they have positive value of SRP) in electrochemical series.

(iii) Elements which get oxidised easily are good reducing agents and elements which get reduced easily are good oxidising agents.

Applications of Electrochemical Series

(i) Metal with lower SRP value displace metal with higher SRP from their solutions. Hence, reactivity of metals decreases from top to bottom in electrochemical series.

(ii) Elements above hydrogen displace hydrogen from any protic solution, whereas elements below hydrogen are unable to displace.

(iii) Thermal stability of metallic oxides decreases down the series due to decrease in electropositive character.

(iv) **To prevent corrosion** Less reactive metals are coated over more reactive metal to prevent corrosion.

(v) **In the extracton of metal** Less electropositive metals are displaced from their ores by adding salt of more electropositive metal.

EMF of a Galvanic Cell

The galvanic cell is made up of two half-cells (anode and cathode). The potential of these half-cells are always different. On account of this difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential, i.e. from cathode to anode. The direction of the flow of electrons is from anode to cathode.

$$\text{Anode} \underset{\text{Flow of current}}{\overset{\text{Flow of electrons}}{\rightleftharpoons}} \text{Cathode}$$

The difference in electrode potentials of the two half-cells is known as the **electromotive force** (emf) of the cell or **cell potential**.

Measurement of EMF

The emf of the cell or cell potential can be measured from the values of electrode potentials of the two half-cells constituting the cell.

The following three methods are in use:

(i) $E°_{cell}$ = oxidation potential of anode + reduction potential of cathode

$$= E°_{oxi} + E°_{red}$$

(ii) $E°_{cell}$ = standard reduction potential of cathode   standard reduction potential of anode

$$= E°_{cathode} \quad E°_{anode} = E°_{right} \quad E°_{left}$$

(iii) $E°_{cell}$ = oxidation potential of anode   oxidation potential of cathode

$$= E°_{oxi}\,(\text{anode}) \quad E°_{oxi}\,(\text{cathode})$$

CHEMISTRY CONCENTRATE

TIPS TO CALCULATE CORRECT CELL POTENTIAL VALUE

In entrance exams, most of the students do common mistakes while solving problems related to calculation of cell potential value. These mistakes can be removed if you follow following conditions :

- You can cross check your final answer whether it is correct or not just by seeing the value of cell potential.
  - → For a forward spontaneous reaction, cell potential value should be positive.
  - → For a backward spontaneous reaction, cell potential value should be negative.
- Mostly we use reduction potential value for both cells for calculating the cell potential value as follow :

$$E_{cell} = E_{cathode} \quad E_{anode} = E_R \quad E_L$$

  → But if oxidation potential of anodic half cell and reduction potential of cathodic half cell is given then E_{cell} is calculated as,

$$E_{cell} = E_{cathode} + E_{anode} = E_R + E_L$$

- If simply potential value is provided along with cell or half cell reaction, this value is considered same as the corresponding phenomena

e.g. $Zn + Cu^{2+}$ ¾ $Zn^{2+} + Cu\,;\ E° = E°_{cell}$

Zn ¾ $Zn^{2+} + 2e\ ;\ E° = E°_{oxidation}$

$Zn^{2+} + 2e$ ¾ $Zn;\ E° = E°_{reduction} = E°_{Zn^{2+}}/Zn$

Best Practice SHOTS

11. In the electrolytic cell, flow of electron is from

(a) cathode to anode in the solution
(b) cathode to anode through external supply
(c) cathode to anode through internal supply
(d) anode to cathode through internal supply

12. E_{cell} is

(a) intensive *(b)* extensive
(c) Both (a) and (b) *(d)* None of these

Hint *E* is an intensive quantity because it depends on the nature of the cell reaction.

13. A gas *X*, at 1 atm is bubbled through a solution containing a mixture of 1 M *Y* and 1 M *Z* at 25° C. If the reduction potential is in the order, $Z > Y >$ X, then

(a) *Y* will oxidise *X* but not *Z* *(b)* *Y* will oxidise *Z* but not *X*
(c) *Y* will oxidise both *X* and *Z* *(d)* *Y* will reduce both *X* and *Z*

Hint Reduction potential of *Y* is greater than that of *X* but less than that of *Z*. Hence, *Y* will oxidise *X* but not *Z*.

14. Standard electrode potentials are:

Fe^{2+}/Fe; $E° =$ 0.44 V, Fe^{3+}/Fe^{2+}; $E° = +$ 0.77 V

Fe^{2+}, Fe^{3+} and Fe blocks are kept together, then

(a) Fe^{3+} increases *(b)* Fe^{3+} decreases
(c) Fe^{2+}/Fe^{3+} remains unchanged
(d) Fe^{2+} decreases

15. $Cr_2O_7^2$ + I ¾ $I_2 + Cr^{3+}$

$E°_{\text{cell}} = 0.79$ V, $E°_{Cr_2O_7^2} = 1.33$ V, $E°_{I_2} = ?$

(a) 0.54 V *(b)* 0.054 V *(c)* + 0.18 V *(d)* 0.18 V

16. The reaction taking place in the cell,

Pt|H_2(*g*)|HCl (1.0) M|AgCl|Ag| is 1 atm

(a) AgCl + $\frac{1}{2}H_2$ ¾ Ag + H^+ + Cl

(b) Ag^+ + H^+ + Cl ¾ AgCl + $\frac{1}{2}H_2$

(c) $2Ag^+$ + H_2 ¾ 2Ag + $2H^+$
(d) 2Ag + $2H^+$ ¾ $2Ag^+$ + H_2

17. The standard reduction potentials at 298 K for the following half cells are given

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s);\ E° = -0.726\,V$$
$$Cr^{3+}(aq) + 3e \rightleftharpoons Cr(s);\ E° = -0.740\,V$$
$$2H^+(aq) + 2e \rightleftharpoons H_2(g);\ E° = 0.000\,V$$
$$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq);\ E° = 0.770\,V$$

Which is the strongest reducing agent?

(a) Cr(s) *(b)* Zn(s) *(c)* H_2(*g*) *(d)* Fe^{2+}(*aq*)

18. On the basis of the following *E*° values, the strongest oxidising agent is

$[Fe(CN)_6]^4$ ¾ $[Fe(CN)_6]^3$ + *e* ; $E° =$ 0.35 V
Fe^{2+} ¾ Fe^{3+} + e^{1}; $E° =$ 0.77 V

(a) $[Fe(CN)_6]^4$ *(b)* Fe^{2+}
(c) Fe^{3+} *(d)* $[Fe(CN)_6]^3$

19. What change occurs when a zinc rod is dipped into a blue coloured copper sulphate solution?

(Given, $E°_{Cu^{2+}/Cu} = +$ 0.34 V, $E°_{Zn/Zn^{2+}} = +$ 0.76 V)
Select the correct, option.

(a) Reaction takes place changing blue $CuSO_4$ to colourless $ZnSO_4$
(b) Reaction takes places changing blue $CuSO_4$ to red coloured $ZnSO_4$
(c) Both are correct
(d) None of the above

20. Which of the following reaction is possible at anode?

(a) $2Cr^{3+}$ + $7H_2O$ ¾ $Cr_2O_7^2$ + $14H^+$
(b) F_2 ¾ 2F + $2e^-$
(c) $\frac{1}{2}O_2$ + $2H^+$ ¾ H_2O
(d) None of the above

NERNST EQUATION, BATTERY AND CORROSION

Nernst Equation

It relates the cell potential of an electrochemical cell to the concentrations of the reactants and products of a chemical reaction at any point of time. For the following reaction at equilibrium,

$$pA + qB + \ldots \rightleftharpoons rX + sY + \ldots$$

Nernst equation is

$$E_{\text{cell}} = E°_{\text{cell}} \quad \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

Applications of the Nernst Equation

(i) **To calculate the value of potential of a concentration cell** A concentration cell is an electrochemical cell in which potential is generated due to difference in concentration of electrolyte in different half cells. As the cell operates, the concentration increases in the dilute half-cell and decreases in concentrated half-cell. We can calculate the generated potential with the help of Nernst equation. e.g. $Zn|Zn^{2+}(C_1)||Zn^{2+}(C_2)|Zn$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{C_2}{C_1},\ [C_2 > C_1;\ E°_{\text{cell}} = 0]$$

CHEMISTRY CONCENTRATE

TRICKS TO SOLVE PROBLEMS RELATED TO CONCENTRATION CELL

Different kinds of problems have been asked in JEE Main and advanced. Generally, it is observed that students get very confuse while solving problems related to concentration cell. But these problems are very easy to solve if we approach the questions stepwise written as below:

***Step* 1** Write down the concentration cell, $M|M^{n+}(\text{conc.})||M^{n+}(\text{dil.})|M$

***Step* 2** If half-reactions are mentioned at cathode and anode, then write the half-cell in which reaction occurs at cathode on RHS in the cell representation. $M|M^{n+}(\text{anode})||M^{n+}(\text{cathode})|M$

***Step* 3** Write down the Nernst equation, for concentration cell,

$$E_{\text{cell}} = E°_{\text{cell}} \quad \frac{2.303\,RT}{nF}\log\frac{[M^{n+}]_{\text{anode (LHS)}}}{[M^{n+}]_{\text{cathode (RHS)}}}$$

$$E_{\text{cell}} = E°_{\text{cell}} \quad \frac{2.303\,RT}{nF}\log\frac{[M^{n+}]_{\text{conc.}}}{[M^{n+}]_{\text{dil.}}}$$

***Step* 4** For concentration cell, $E°_{\text{cell}} = 0$, put this value in Nernst equation, $E_{\text{cell}} = \dfrac{2.303\,RT}{nF}\log\dfrac{[M^{n+}]_{\text{LHS}}}{[M^{n+}]_{\text{RHS}}}$

***Step* 5** Find out the required quantity with the help of Nernst equation.

***Step* 6** If solubility product (K_{sp}) is asked to find out, then determine the concentrations of M^{n+} and X^{m} .

***Step* 7** Determine solubility product as $K_{\text{sp}} = (mS)^m(nS)^n$.

(ii) **Determination of solubility products** The concentrations of ions in equilibrium with a sparingly soluble salt are sufficiently low and the Nernst equation can be used to determine the value of K_{sp}.

(iii) **Potentiometric titrations** In many situations, accurate determination of an ion concentration by direct measurement of a cell potential is impossible due to the presence of other ions and a lack of information about activity coefficients. In such cases, it is often possible to determine the ion indirectly by titration with some other ion by the help of Nernst equation.

(iv) **Measurement of pH** A hydrogen electrode allows a direct measurement of $[H^+]$ and thus pH is given as

$$\text{pH} = \frac{E_{\text{cell}} \quad E°_{\text{reference}}}{0.0591}$$

Relationship between Standard Potentials of Half-cells Containing a Metal in Different Oxidation State

- If two half-reactions having potentials E_1° and E_2° are combined to form a third half-reaction having a potential E_3°, then we can write

$$G°_3 = G°_1 + G°_2 \text{ or } n_3FE_3^\circ = n_1FE_1^\circ \quad n_2FE_2^\circ$$

$$\text{or } n_3E_3^\circ = n_1E_1^\circ + n_2E_2^\circ \text{ or } E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$$

Note A reaction will be feasible if, $G < 0$, $E_{\text{cell}} > 0$.

CHEMISTRY CONCENTRATE

FORMULAE OF THERMODYNAMIC QUANTITIES IN ELECTROCHEMISTRY

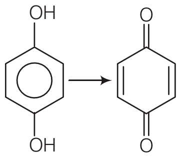
- Maximum work done by a cell, $W_{\text{max}} = nFE°_{\text{cell}}$
- Gibbs free energy change of a cell, $G = \quad nFE_{\text{cell}}$
- Temperature coefficient of emf of a cell reaction,

$$\text{æ}\text{ç}\frac{dE_{\text{cell}}}{dT}\text{ö}\text{÷}_P = \frac{H}{nFT} + \frac{E_{\text{cell}}}{T}$$

- Enthalpy change, $H = \quad nF\ E_{\text{cell}} \quad T\text{æ}\text{ç}\dfrac{dE_{\text{cell}}}{dT}\text{ö}\text{÷}_P$
- Entropy change, $S = nF\text{æ}\text{ç}\dfrac{dE_{\text{cell}}}{dT}\text{ö}\text{÷}_P$
- Relation between G and K_C $\quad G = \quad G° + 2.303RT\log Q$

  At equilibrium, $G = 0$ and $K_C = Q$ $\quad G° = \quad 2.303RT\log K_C$

Various reference half-cell reactions showing Nernst equation

	Type	Example	Half-cell reaction	Q	Reversible to	Electrode potential (*E*) (oxidation),
1.	Gas-ion half-cell	$\text{Pt}(H_2)\|H^+(aq)$	$\frac{1}{2}H_2(g)\ \text{¾}\ H^+(aq)+e$	$[H^+]$	H^+ ion	$E° \quad 0.0591\log[H^+]$
		$\text{Pt}(Cl_2)\|Cl\ \ (aq)$	$Cl\ \ (aq)\ \text{¾}\ \frac{1}{2}Cl_2(g)+e$	$\frac{1}{[Cl\ \ ]}$	Cl ion	$E° + 0.0591\log[Cl\ \ ]$
2.	Metal-metal ion half-cell	$Ag\|Ag^+(aq)$	$Ag(s)\ \text{¾}\ Ag^+(aq)+e$	$[Ag^+]$	Ag^+ ion	$E° \quad 0.0591\log[Ag^+]$
3.	Metal-insoluble salt anion half-cell	$Ag, AgCl\|Cl\ \ (aq)$	$Ag(s)+Cl\ \ (aq)\ \text{¾}\ AgCl(s)+e$	$\frac{1}{[Cl\ \ ]}$	Cl ion	$E° + 0.0591\log[Cl\ \ ]$
4.	Calomel electrode	$Hg, Hg_2Cl_2\|Cl\ \ (aq)$	$2Hg(l)+2Cl\ \ (aq)\ \text{¾}\ Hg_2Cl_2(s)+2e$	$\frac{1}{[Cl\ \ ]^2}$	Cl ion	$E° + 0.0591\log[Cl\ \ ]$
5.	Metal-metal oxide hydroxide half-cell	$Hg, HgO\|\bar{O}H\ (aq)$	$Hg(l)+2OH\ \ (aq)\ \text{¾}\ HgO(s)+H_2O(l)+2e$	$\frac{1}{[OH\ \ ]^2}$	OH ion	$E° + 0.0591\log[OH\ \ ]$
6.	Oxidation-reduction half-cell	$\text{Pt}\|Fe^{2+}(aq), Fe^{3+}(aq)$	$Fe^{2+}(aq)\ \text{¾}\ Fe^{3+}(aq)+e$	$\frac{[Fe^{3+}]}{[Fe^{2+}]}$	Fe^{2+}, Fe^{3+} ion	$E° \quad 0.0591\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$
7.	Mercury-mercury sulphate half-cell	$Hg, HgSO_4\|SO_4^2\ \ (aq)$	$SO_4^2\ \ (aq)+Hg(l)\ \text{¾}\ HgSO_4(s)+2e$	$\frac{1}{[SO_4^2\ \ ]}$	SO_4^2	$E° + \frac{0.0591}{2}\log[SO_4^2\ \ ]$
8.	Quinhydrone half-cell	Pt|Quinhydrone| $H^+(aq)$	 $+2H^+ + 2e^-$	$[H^+]^2$	H^+	$E° \quad 0.0591\log[H^+]$

{JEE FINAL TOUCH}

Cell or Battery

A cell or a battery (arrangement of one or more cells connected in series) is basically a galvanic cell where the chemical energy of redox reaction is converted into electrical energy.

Following are the various voltaic cells:

Primary Voltaic Cell (The Dry Cell)

The primary voltaic cells are those in which the cell reaction occurs only once and the cell becomes dead after use over a period of time and cannot be reused again, e.g. dry cells like Leclanche cell, mercury cell etc.

(i) **Leclanche cell** The electrode reaction for Leclanche cell is

At anode $Zn(s)$ ¾ $Zn^{2+} + 2e$

At cathode

$MnO_2 + NH_4^+ + e$ ¾ $MnO(OH) + NH_3$

Ammonia (NH_3) formed in reaction at cathode combines with Zn^{2+} to form the complex like $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

(ii) **Mercury cell** It shows the following electrode reactions:

At anode $Zn(Hg) + 2OH$ ¾ $ZnO(s) + H_2O + 2e$

At cathode $HgO(s) + H_2O + 2e$ ¾ $Hg(l) + 2OH$

The overall reaction is

$Zn(Hg) + HgO(s)$ ¾ $ZnO(s) + Hg(l)$

The potential of this cell is approximately 1.35 V and it remains constant during its life because overall reaction does not involve any ion whose concentration can change during the process.

Secondary Voltaic Cell

The cell in which original reactants are regenerated by passing direct current from external source (recharged), is called secondary cell.

(i) **Lead accumulator** (lead storage battery) The most important secondary voltaic cell is lead storage battery, commonly used in automobiles and invertors.

A 38% solution of H_2SO_4 is used as electrolyte.

The reaction taking place during discharging [when cell is in use] is

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

¾ $2PbSO_4(s) + 2H_2O(l)$

Reverse reaction occurs when cell is charged E_{cell} is 2.041 V.

(ii) **Nickel cadmium battery** Another important secondary battery is Ni-Cd battery with longer life but more expensive. The overall reaction during discharge is

$Cd(s) + 2Ni(OH)_3(s)$ ¾ $CdO(s)$

$+ 2Ni(OH)_2(s) + H_2O(l)$

The reverse reaction occurs when cell is charged.

Batteries Used in Digital Watches

- Several watch batteries (button cells) used mercury technology until a few years ago but mercury is highly toxic and there is no reasonable way to safely extract and recycle the mercury in watch batteries. Hence, this technology is not used now because of environmental reasons.
- Now a days, silver oxide technology is used for high quality batteries of watches because these are most efficient when squeezing the last bit of electricity into a confined space for storage.
- Over time, watch industry has added new features such as background lighting, audible alarms or even feature calculators. This has lead to the development of additional high drain versions of watch batteries to feed the extra requirement of power.
- A few brands are considered as the best by fine watchmakers and are popular choices as replacement batteries. They include Renata, Maxwell, Varta, Sony and Energizer batteries.

Fuel Cells

Galvanic cells which use energy of combustion of fuels like H_2, CH_4, CH_3OH etc., as the source to produce electrical energy are called fuel cells. One of the most successful fuel cell uses the energy of reaction of H_2 and O_2 in gaseous state to form water. The electrode reactions for the cell are :

At anode $2H_2(g) + 4OH(aq)$ ¾ $4H_2O(l) + 4e$

At cathode $O_2(g) + 2H_2O(l) + 4e$ ¾ $4OH(aq)$

The overall reaction is

$2H_2(g) + O_2(g)$ ¾ $2H_2O(l)$

This type of cell runs continuously as long as the fuels are supplied and produce electricity up to 70% efficiency. The advantage of fuel cells over batteries is that these are pollution free and highly efficient.

Some Other Fuel Cells

1. **Phosphoric acid fuel cell** Liquid H_3PO_4 is used as an electrolyte. This is the first fuel cell to be commercialised.

   Anode reaction $2H_2$ ¾ $4H^+ + 4e$

   Cathode reaction $O_2(g) + 4H^+ + 4e$ ¾ $2H_2O$

2. **Alkaline fuel cell** It is one of the most efficient fuel cell, used by NASA since mid 1960s to propagate launching verticles.

   Anode reaction $2H_2 + 4OH$ ¾ $4H_2O + 4e$

   Cathode reaction $O_2 + 2H_2O + 4e$ ¾ $4OH$

3. **Molten carbonate fuel cell** This can operate at extreme high temperature of 600°C and above. It is generally used for industrial purpose.

   Anode reaction $H_2 + CO_3^2 \rightleftharpoons H_2O + CO_2 + 2e$

   Cathode reaction $CO_2 + \frac{1}{2}O_2 + 2e \rightleftharpoons CO_3^2$

4. **Direct methanol fuel cell** Methanol is used as fuel.

   Anode reaction $CH_3OH + H_2O \rightleftharpoons 6H^+ + 6e + CO_2$

   Cathode reaction $\frac{3}{2}O_2 + 6H^+ + 6e \rightleftharpoons 3H_2O$

Corrosion

It is the oxidative deterioration of metal surface with the action of its environment to form unwanted corrosion products like oxides, sulphides, carbonates, sulphates.

It usually affects metallic substances and typically produce oxide(s) or salt(s) of metal, e.g. conversion of iron to rust $[Fe_2O_3 \cdot xH_2O]$, the tarnishing of silver (due to the formation of Ag_2O), development of a green coating on copper and bronze.

Corrosion of iron or rusting involves the following reactions:

Oxidation half-cell $2Fe(s) \quad 2Fe^{2+} + 4e \; ; E^{\circ}_{(Fe^{2+}/Fe)} = -0.44V$

Reduction half-cell $O_2(g) + 4H^+(aq) + 4e \longrightarrow 2H_2O(l);$

$$E^{\circ}_{(H^+/O_2/H_2O)} = 1.23V$$

Overall reaction

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l);$$

$$E^{\circ}_{cell} = 1.67 \text{ V}$$

Ferrous ions, Fe^{2+} undergo oxidation with O_2 to form rust $[Fe_2O_3 \cdot xH_2O]$.

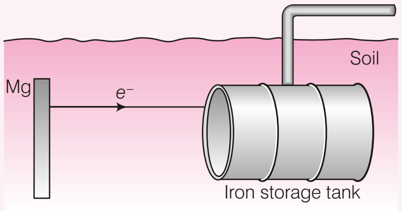
$$2Fe^{2+} + 2H_2O + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 4H^+ \xrightarrow{H_2O} \underset{\substack{\text{(Rust)} \\ \text{Hydrated ferric oxide}}}{Fe_2O_3 \cdot xH_2O}$$

Prevention of Rusting

The followings are the most effective way of preventing rusting:

(a) **Galvanisation** In galvanisation, a thin film of Zn is coated over iron, where Zn forms a protective oxide layer. Even if the zinc coating breaks down and iron is exposed to air, Zn reduces Fe^{2+} back to Fe(s), as reduction potential of Fe is more than that of Zn.

(b) **Cathodic protection** Here, the equipment made of Fe is attached to a more easily oxidisable metal like Mg. Here, Mg acts as a sacrificial anode, as it reacts in preference to iron. The Mg rod should be replaced periodically.



$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e$ Oxidation

$O_2(g) + 2H_2O(l) + 4e \longrightarrow 4OH \; (aq)$ Reduction

Best Practice SHOTS

21. The following cell is found to have emf equal to zero
$Pt, H_2 \; (x \, atm) \mid 0.01 \; MH^+ \| \; 0.1 \; MH^+ \mid H_2 (y \, atm), \; Pt$
The ratio x/y is

(a) 0.01 (b) 0.1
(c) 10 (d) 100

22. If Zn^{2+}/Zn electrode is diluted 100 times, then the change in emf is

(a) increase by 59 mV
(b) decrease by 59 mV
(c) increase by 29.5 mV
(d) decrease by 29.5 mV

Hint $E_{cell} = E^{\circ}_{cell} \quad \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$

$= E^{\circ}_{cell} + 0.0295 \log [Zn^{2+}]$

After dilution $E_{cell} = E^{\circ}_{cell} + 0.0295 \log \frac{[Zn^{2+}]}{100}$

E_{cell} will decrease by $0.02955 \quad 2 \text{ V} = 0.059 \text{ V} = 59 \text{ mV}$

23. Which one of the following statement is always true about the spontaneous cell reaction in a galvanic cell?

(a) $E^{\circ}_{cell} > 0, \quad G^{\circ} > 0, Q > K_C$
(b) $E^{\circ}_{cell} < 0, \quad G^{\circ} < 0, Q < K_C$
(c) $E^{\circ}_{cell} > 0, \quad G^{\circ} < 0, Q < K_C$
(d) $E^{\circ}_{cell} > 0, \quad G^{\circ} < 0, Q > K_C$

24. When a lead storage battery is discharged

(a) SO_2 is evolved
(b) lead is formed
(c) lead sulphate is consumed
(d) sulphuric acid is consumed

25. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because

(a) Zn acts as oxidising agent when reacts with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) In electrochemical series, Zn is above hydrogen
(d) NO_3 is reduced in preference to hydronium ion

26. The emf (E) of a cell is related to its variation in temperature $\left(\frac{E}{dT}\right)_p$ and H as

(a) $E = \frac{H}{nF} + T\left(\frac{E}{T}\right)_p$ (b) $E = \frac{H}{nF} \quad T\left(\frac{E}{T}\right)_p$
(c) $E = \quad \frac{H}{nF} + T\left(\frac{E}{T}\right)_p$ (d) $E = \quad \frac{H}{nF} \quad T\left(\frac{E}{T}\right)_p$

27. For the cell reaction,

$$Cu^{2+}(C_1, aq) + Zn(s) \longrightarrow Zn^{2+}(C_2, aq) + Cu(s)$$

of an electrochemical cell, the change in free energy, G, at a given temperature is a function of

(a) $\ln C_1$ (b) $\ln C_2/C_1$ (c) $\ln C_2$ (d) $\ln(C_1 + C_2)$

28. The temperature coefficient of a galvanic cell is $+5.0 \quad 10^{5}$ mV/K. During the discharge of the cell, the cell temperature?

(a) increases (b) decreases (c) does not change
(d) first increases and then decreases

29. The potential of hydrogen electrode at pH = 10 is

(a) 0.59 V (b) 0.00 V (c) 0.59 V (d) 0.059 V

Hint $E = \quad 0.0591 \quad pH$

{JEE FINAL TOUCH}

30. At what pH of HCl solution will hydrogen gas electrode potential of 0.118 V? H_2 gas is bubbled at 298 K and 1 atm pressure

(a) 2	*(b)* 3
(c) 4	*(d)* 5

31. In an experiment 0.04 F was passed through 400 mL of 1M solution of NaCl. What would be the pH of the solution after the electrolysis?

(a) 8	*(b)* 10
(c) 13	*(d)* 6

Hint Find molar concentration of NaOH

Find [OH] concentration pH = 14 pOH

32. The potential of the cell for the reaction,

$$M(s) + 2H^+ (1\,M) \ ¾ \ \underset{(1\text{ atm})}{H_2(g)} + \underset{(0.1\text{ M})}{M^{2+}}$$

is 1.50 V. The standard reduction potential for $M^{2+} / M(s)$ couple is

(a) 0.147 V	*(b)* 1.47 V
(c) 1.47 V	*(d)* None of these

33. The half-cell reactions for rusting of iron are

$$2H^+ + \frac{1}{2}O_2 + 2e \ ¾ \ H_2O;\ E° = +1.23\text{ V}$$

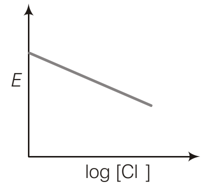
$$Fe^{2+} + 2e \ ¾ \ Fe\ (s);\ E^{\circ}_{cell} = \ 0.44\text{ V}$$

 $G°$ (in kJ) for the reaction is

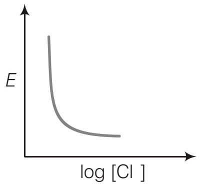
(a) 76 *(b)* 322 *(c)* 122 *(d)* 176

34. For the calomel electrode, $Hg, Hg_2Cl_2|Cl^{\ }(aq)$, electrode potential measured at different Cl ion concentration are plotted against log[Cl]. The variation is correctly represented by plot.

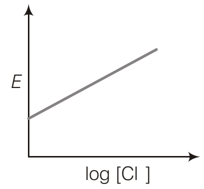
(a)



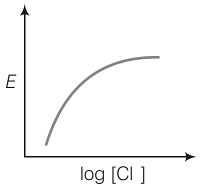
(b)



(c)



(d)



Hint From equation,

$$2Hg(l) + 2Cl^{\ }(aq) \ ¾ \ Hg_2Cl_2(s) + 2e$$

$$E = E° \ \frac{0.0591}{2} \log \frac{1}{[Cl^{\ }]^2}$$

or compare this equation with $y = mx + c$
$E = E° + 0.0591 \log[Cl^{\ }]$.

35. Value of $E_{H_2O/H_2(1\text{ atm})\,pt}$ at 298 K would be

(a) 0.207 V *(b)* + 0.207 V *(c)* 0.414 V *(d)* + 0.414 V

Hint $E = \ \dfrac{RT}{F} \ln \dfrac{p_{H_2}^{1/2}}{[H^+]}$

Answers

1. (d)	**2.** (d)	**3.** (c)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (a)	**9.** (c)	**10.** (b)
11. (b)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (a)	**17.** (b)	**18.** (c)	**19.** (a)	**20.** (a)
21. (a)	**22.** (b)	**23.** (c)	**24.** (d)	**25.** (d)	**26.** (c)	**27.** (b)	**28.** (b)	**29.** (c)	**30.** (a)
31. (c)	**32.** (c)	**33.** (b)	**34.** (c)	**35.** (c)					

MASTER STROKE

1. The equivalent conductance at infinite dilution of HCl and NaCl are 426.15 and 126.15 mho $cm^2 g\text{-}eq^{\ 1}$ respectively. It can be said that the mobility of

(a) H^+ ions is much more than that of $Cl^{\ }$ ions
(b) $Cl^{\ }$ ions is much more than that of H^+ ions
(c) H^+ ions is much more than that of Na^+ ions
(d) Na^+ ions is much more than that of H^+ ions

Hint $\ ^{\circ}_{eq}(HCl) >> \ ^{\circ}_{eq}(NaCl)$.

As, $Cl^{\ }$ ions are common, this implies that ionic conductance of H^+ >> ionic conductance of Na^+ ions.

As ionic conductance ionic mobility. ($_{cation}$ µ $_{cation}$, ($_{anion}$ µ $_{anion}$), therefore, H^+ ions have much greater mobility than Na^+ ions.

2. What is the potential of a zinc-zinc ion electrode in which the zinc ion activity is 0.001 M?

($E°_{Zn^{2+}/Zn}$ = 0.76 V, R = 8.314 J/K mol, F = 96500 C mol)

(a) 0.648 V *(b)* 0.849 V *(c)* + 0.648 V *(d)* + 0.849 V

Hint $E = E° \ \dfrac{2.303RT}{nF} \log \dfrac{1}{a_{Zn^{2+}}}$

3. Half-cell reaction, $2H_2O + 2e \ ¾ \ H_2 + 2OH$

$E° = \ 0.8277$ V at 298 K

Auto-protolysis constant of water calculated from this value will be

(a) 1 $10^{\ 10}$	*(b)* 1 $10^{\ 12}$
(c) 1 $10^{\ 13}$	*(d)* 1 $10^{\ 14}$

4. What will be the emf of the given cell?

$$Pt|H_2(p_1)|H^+(aq)|H_2(p_2)|Pt$$

(a) $\frac{RT}{F}\ln\frac{p_1}{p_2}$ (b) $\frac{RT}{2F}\ln\frac{p_1}{p_2}$

(c) $\frac{RT}{F}\ln\frac{p_2}{p_1}$ (d) None of these

5. $\overset{\circ}{}_{eq}$ for $BaCl_2$, H_2SO_4 and HCl are x_1, x_2 and x_3 Scm^2 $eq^{\ 1}$ respectively. If conductivity of saturated $BaSO_4$ solution is y $Scm^{\ 1}$, then K_{sp} for $BaSO_4$ is

(a) $\frac{10^6 y^2}{2(x_1 + x_2 \quad 2x_3)}$

(b) $\frac{10^9 y^3}{8(x_1 + x_3 \quad 2x_3)^3}$

(c) $\frac{10^3 y}{2(x_1 + x_2 \quad 2x_3)}$

(d) $\frac{10^6 y^2}{4(x_1 + x_2 \quad 2x_3)^2}$

Hint $\overset{\circ}{}_{eq}(BaSO_4) = \overset{\circ}{}_{eq}(BaCl_2) + \overset{\circ}{}_{eq}(H_2SO_4) \quad 2\ \overset{\circ}{}_{eq}(HCl)$

$= x_1 + x_2 \quad 2x_3$

$$\overset{\circ}{}_{eq}(BaSO_4) = \frac{1000}{\text{Normality}}$$

$$\text{Solubility} = \frac{1000 \quad y}{x_1 + x_2 \quad 2x_3};\ K_{sp} = [Ba^{2+}][SO_4^{2}\ ] = S^2$$

6. Which has maximum potential for the half-cell reaction?

$$2H^+ + 2e \quad ¾ \quad H_2$$

(a) 1.0 M HCl (b) 1.0 M NaOH

(c) Pure water (d) A solution with pH = 4

7. How many moles of Pt may be deposited on cathode when 0.80 F of electricity is passed through 1.0 M solution of Pt^{4+}?

(a) 1 mol (b) 0.20 mol (c) 0.40 mol (d) 0.80 mol

8. Given the standard reduction potential ($E°$) value of

$$Fe^{3+} + e \quad ¾ \quad Fe^{2+};\ E° = 0.77\ V$$
$$Fe^{3+} + 3e \quad ¾ \quad Fe;\ E° = \quad 0.04\ V$$

What is the value of $E°$ for $Fe^{2+} + 2e$ ¾ Fe?

(a) 0.730 V (b) 0.195 V (c) 0.445 V (d) 0.89 V

9. Which of the following statement is correct?

(a) More reactive metals are readily corroded
(b) Corrosion takes place rapidly at bends, scratches, nicks and cuts in the metal
(c) Presence of impurities in metals enhances the chances of corrosion
(d) All of the above

10. Which of the following reaction takes place in fuel cell?

(a) $2H_2(g) + O_2(g)$ ¾ $2H_2O(l)$
(b) $2H_2O(l)$ ¾ $2H_2(g) + O_2(g)$
(c) $2H_2O(l) + H_2(g)$ ¾ $OH(aq)$
(d) None of the above

11. The amount of an ion liberated on an electrode during electrolysis does not depend upon

(a) the conductance of the solution
(b) current strength
(c) time
(d) electrochemical equivalent of the element

12. E_1, E_2 and E_3 are the emf values of the three galvanic cells respectively are

(i) $Zn|Zn^{2+}(1\ M)||Cu^{2+}(0.1\ M)|Cu$
(ii) $Zn|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu$
(iii) $Zn|Zn^{2+}(0.1\ M)||Cu^{2+}(0.1\ M)|Cu$

Which one of the following is true?

(a) $E_2 > E_3 > E_1$ (b) $E_3 > E_2 > E_1$

(c) $E_1 > E_2 > E_3$ (d) $E_1 > E_3 > E_2$

Hint Use Nernst equation.

13. The standard emf of a cell, involving one electron change is found to be 0.591 V at 25°C.

The equilibrium constant of the reaction is

($F = 96500\ C\ mol^{\ 1}$; $R = 8.314\ JK^{\ 1}mol^{\ 1}$)

(a) $1.0 \quad 10^1$ (b) $1.0 \quad 10^{30}$

(c) $1.0 \quad 10^{10}$ (d) $1.0 \quad 10^5$

14. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are

(a) O_2, H_2 (b) SO_2, Na

(c) O_2, Na (d) $S_2O_8^{2}$, H_2

Hint H_2O is more readily reduced than Na^+. It is also more readily oxidised than SO_4^{2}.

15. Resistance of 0.2 M solution of an electrolyte is 50 . The specific conductance of the solution of 0.5 M solution of same electrolyte is 1.4 $S\,m^{\ 1}$ and resistance of same solution of the same electrolyte is 280 . The molar conductivity of 0.5 M solution of the electrolyte in $Sm^2mol^{\ 1}$ is

(a) $5 \quad 10^{\ 4}$ (b) $5 \quad 10^{\ 3}$

(c) $5 \quad 10^3$ (d) $5 \quad 10^2$

Hint Calculate the value of cell constant of the first solution.

- Use this value of cell constant to calculate of second solution.
- Finally calculate molar conductivity using value of and *M*.

Answers

1. (c) **2.** (b) **3.** (d) **4.** (b) **5.** (d) **6.** (a) **7.** (b) **8.** (c) **9.** (d) **10.** (a)
11. (a) **12.** (b) **13.** (c) **14.** (a) **15.** (a)

Chemical Kinetics

RATE OF A CHEMICAL REACTION, DIFFERENTIAL RATE LAW AND FACTORS AFFECTING RATE OF A REACTION

Chemical kinetics is the branch of chemistry in which we study about the speeds of reactions or rearrangements by which atoms and molecules are transformed from reactants to products.

Rate of a Chemical Reaction

It is defined as the change in concentration of a reactant or product per unit time.

Types of Rates of a Reaction

(a) **Average rate** It is defined as change in molar concentration of either reactants or products in unit time.

(b) **Instantaneous rate** It is the slope of a line tangent drawn on the concentration-time curve at the point corresponding to the specific concentration and time.

Factors Affecting Rate of a Reaction

- **Concentration of reactants** It is directly proportional to the rate of reaction.
- **Nature of the reactants**
  Physical state of reactants

  Gaseous state > Liquid state > Solid state

  Decreasing rate of reaction

Physical size of the reactants In solids, rate increases with decrease in particle size because in powdered state, particles possess larger surface area.

- **Temperatures** Generally for most of the reactions rate becomes double for every 10°C rise in temperature.
- **Presence of catalyst** Positive catalyst increases however negative catalyst decreases the rate of a reaction.

Rate Expression and Rate Constant (k)

An expression which relates the rate of a reaction to the concentrations of the reactants is called the rate expression. For a general reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} \propto [A]^a\,[B]^b \text{ or Rate} = k\,[A]^a\,[B]^b$$

The constant of proportionality, k is known as the rate constant.

Note k depends on the temperature and is independent of the initial concentrations of the reactants.

Molecularity of a Reaction

It is defined as the numbers of particles (atoms, ions, groups or molecules) of reactants actually taking part in a single rate determining step of a chemical reaction. On the basis of molecularity reactions are of three types:

(i) **Unimolecular** involves participation of only one molecule.
e.g. $O_2F_2 \rightleftharpoons O_2 + F_2$

(ii) **Bimolecular** involves participation of two molecules.
e.g. $2HI \longrightarrow H_2 + I_2$

(iii) **Trimolecular** involves participation of three molecules .
e.g. $2NO + Cl_2 \longrightarrow 2NOCl$

REMEMBER

- Molecularity of a reaction is always a whole number (except zero) and never a fraction.
- The value of molecularity of a simple or one step reaction does not exceed more than three because probability of colloiding more than three molecules is almost negligible.

Order of a Reaction

It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate equations.

- For a zero or
- der reaction, rate does not depend upon the concentration of reactant.
- For a nth order reaction, rate depends upon the nth power of concentration. e.g. $nA \longrightarrow$ Products

For $n = 0$; rate $= k$; Zero order reaction.
For $n = 1$; rate $= k[A]$; First order reaction.
For $n = 2$; rate $= k\,[A]^2$; Second order reaction.
For $n = n$; rate $= k\,[A]^n$; nth order reaction.

Relevance of Chemical Kinetics in Medicine

- Nitric oxide (NO), is central to many physiological processes including regulation of blood pressure and nerve signal transmission. Enzymes in endothelial cells and in the brain of mammals continuously synthesise it (generally in low and carefully regulated concentrations). NO reacts with oxygen and produce toxic nitrogen dioxide (NO_2).
- The order of this reaction is two with respect to NO. High concentrations of NO are found often in industrial plants and cigarettes. NO reacts rapidly with oxygen to produce toxic NO_2.
- The half-life of NO in blood vessels, brain and lungs is sufficiently long for biochemical process. Kinetics determines the harmful and helpful aspects of nitric oxide. At concentrations below 80 ppm. NO is used in hospitals for lung vasodilation of preterm new borns and patients with **Acute Respiratory Distress Syndrome** (ARDS).

Methods for Determination of Order of Reaction

Initial rate method In this method, the order of a reaction is determined by varying the concentration of one of the reactants, while keeping others constant, e.g.

$$aA + bB \longrightarrow \text{Product}$$

$$r = k\,[A]^a[B]^b$$

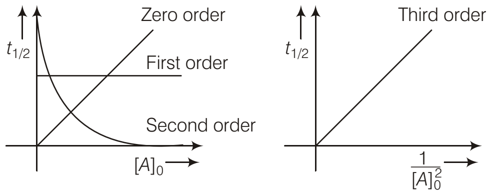
If $[B]$ remains constant, $r = k^1\ [A]^a$, where, $k^1 = k\ [B]^b$

The value of a can be determined by inspecting the rate at different concentrations of A.

Integration method Also called hit and trial method. In this method, different values of $[A]_0$, $[A]_t$ and t are determined experimentally and substituted in rate equation of various order.

Half-life method It is also called fractional change method. For a reaction of nth order, $t_{1/2} \propto (1/[A]_0)^{n \quad 1}$ or $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{[A_0]_2}{[A_0]_1}\right)^{n \quad 1}$

Taking logarithm on both sides, $n = 1 + \frac{\log[(t_{1/2})_1 / (t_{1/2})_2]}{\log\{[A_0]_2/[A_0]_1\}}$



$$t_{\text{av}} = \frac{1}{k} \text{ and for first order reaction, } t_{\text{av}} = 1.44\, t_{1/2}$$

Graphical method In this method, the order of reaction can be obtained by plotting a graph between $\log\left(\frac{dx}{dt}\right)$ *versus* $\log [A]_t$ or $\log (a \quad x)$.

Note There are some reactions which show fractional and negative orders.

e.g. $CO + Cl_2 \longrightarrow COCl_2$; rate $= k[CO]^2[Cl_2]^{1/2}$; order = 2.5

$2O_3 \longrightarrow 3O_2$; rate $= k[O_3]^2[O_2]^{\ 1}$; order with respect to O_2 is 1.

Formulae Related to the Rate and Order of a Reaction

- For a general reaction,

  $$aA + bB \longrightarrow cC + dD$$

  $$\text{Rate } (r) = \ \frac{1}{a}\frac{\ [A]}{\ t} = \ \frac{1}{b}\frac{\ [B]}{\ t} = \frac{1}{c}\frac{\ [C]}{\ t} = \frac{1}{d}\frac{\ [D]}{dt}$$
- **Average rate** $r_{\text{av}} = \ \frac{\ [R]}{\ t} = \frac{\ [P]}{\ t}$
- **Instantaneous rate** $r_{\text{ins}} = \lim_{\ t \quad 0} \ \frac{\ [C]}{\ t} = \ \frac{d[C]}{dt}$; $[C]$ = conc. of reactant

  $d[C]$ = Change in the concentration of reactant in infinitesimally small interval of time dt.
- **Differential rate equation** rate $= k[A]^x[B]^y$

  where, x and y are calculated experimentally.
- **Order of a chemical reaction** $x + y$ (experimentally)
- **Order of an elementary chemical reaction** $a + b$

Best Practice SHOTS

1. The correct relation in between $\frac{dC}{dt}$, $\frac{dn}{dt}$ and $\frac{dp}{dt}$ where, C, n and p represent concentration, number of moles and pressure of gaseous reactant, $A(g) \longrightarrow$ Product, is

(a) $\ \frac{dC}{dt} = \ \frac{1}{V}\frac{dn}{dt} = \ \frac{1}{RT}\frac{dp}{dt}$ (b) $\frac{dC}{dt} = \frac{RT}{V} \times \frac{dn}{dt} = \ \frac{dp}{dt}$

(c) $\frac{dC}{dt} = \frac{dn}{dt} = \ \frac{dp}{dt}$ (d) All of these

Hint (i) Rate $= \ \frac{dC}{dt} = \ \frac{1}{V}\left(\frac{dn}{dt}\right)\ \left\{\because C = \frac{n}{V}\right\}$

(ii) Rate $= \ \frac{dC}{dt} = \ \frac{1}{RT} \times \left(\frac{dp}{dt}\right); \left\{\because C = \frac{p}{RT}\right\}$

2. For the sequence of reactions, $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$

If $k_3 > k_2 > k_1$, then rate determining step is

(a) $A \quad B$ (b) $B \quad C$ (c) $C \quad D$ (d) $A \quad D$

3. Temperature coefficient of a reaction is 2. What will be the rate of reaction when temperature increases from 30°C to 100°C?

(a) 120 times (b) 150 times (c) 128 times (d) 100 times

Hint Increase in rate $= 2^{(T_2 \quad T_1)/100}$ times.

4. For the reaction, $O_3 \rightleftharpoons O_2 + O$ (fast)

$$O + O_3 \longrightarrow 2O_2 \text{ (slow)}.$$

The rate law is

(a) $r = k\ [O_3]^2[O_2]^{\ 1}$ (b) $r = k\ [O_3]$

(c) $r = k\ [O_3][O]^2$ (d) $r = [O_3]^2[O]$

5. For a gaseous reaction, the rate law is $r = k[A]^2\,[B]$. If volume of reaction decreases to 1/3rd of initial volume, the new concentration and order of reaction respectively becomes,

(a) rate will increase by 27 times and order remains same

(b) rate will decrease by 27 times and order remains same

(c) rate will increase by 27 times and order becomes $\frac{1}{3}$rd of its initial order

(d) show no change in rate or order

Hint When volume decreases to $V/3$ rate becomes

$$r\ = k\ \frac{A}{V/3}^{\ 2}\ \frac{B}{V/3}$$

{JEE FINAL TOUCH}

6. Hydrogenation of vegetable ghee at 25°C reduces pressure of H_2 (g) from 2 atm to 1.2 atm in 50 min. The rate of reaction in terms of change in molarity per second is

(a) $1.19 \quad 10^{6}$ (b) $1.19 \quad 10^{5}$ (c) $1.19 \quad 10^{7}$ (d) $1.19 \quad 10^{8}$

Hint Change in molarity is, $\frac{n}{V}, \frac{n}{V} = \frac{p}{RT}$

7. Half-lives of two samples are 0.1 and 0.8 s. Their respective concentrations are 400 and 50 mol L^{1}. The order of reaction is

(a) 0 (b) 2 (c) 1 (d) 4

8. The rate of reaction is doubled when temperature increases by 10° C, if temperature is increased by 100°C then rate of reaction will become

(a) 64 times (b) 256 times (c) 512 times (d) 1024 times

Hint Rate becomes 2^{10} times

9. Which one of the following statements is not correct for order of reaction?

(a) Order is determined experimentally
(b) Order of reaction is equal to sum of the powers of concentration terms in experimentally determined differential rate law
(c) It is not affected with stoichiometric coefficient of the reactant
(d) Order cannot be fractional

10. In a reversible reaction, the rate of backward reaction is

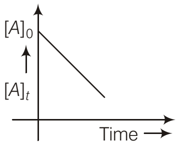
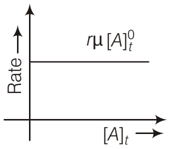
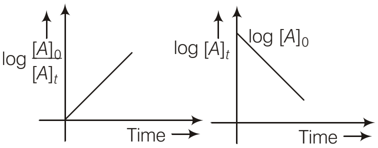
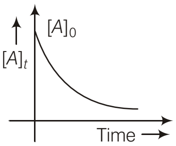
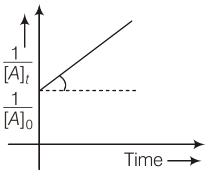
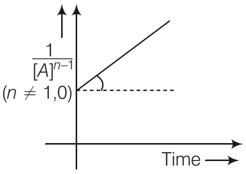
(a) positive (b) negative
(c) zero (d) can not be predicted

Hint Rate of reaction can never be negative.

INTEGRATED RATE LAWS AND VARIOUS FIRST ORDER REACTIONS

It is an approach to determine rate law and rate constant for a reaction by using calculus to derive what is called the integrated rate law.

Different integrated laws for different orders of reaction

Order of reaction	Graphs	Rate expression	Half-life ($t_{1/2}$)	Unit of rate constant	Examples
Zero order	 	$[A]_t = [A]_0 \quad kt$	$\frac{[A]_0}{2k}$	mol $L^{1}s^{1}$	Photochemical reaction, enzyme catalysed reactions etc.
First order reaction	 	$[A]_t = [A]_0 e^{kt}$, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$ $k = \frac{2.303}{t}\log\frac{p_0}{p_0 \quad p_x}$ (for gaseous reaction) time required to complete 1/*n*th of a reaction, $t = \frac{2.303}{k}\log$ æ ç $\frac{n}{n \quad 1}$ ö ÷	$\frac{0.693}{k}$	s^{1}	Radioactive disintegration, regeneration of bacteria etc.
Second order reaction		(i) $kt = \frac{1}{[A]_t} \quad \frac{1}{[A]_0}$, when both reactants have same initial concentrations (ii) $k = \frac{2.303}{t(a \quad b)}\log\frac{b(a \quad x)}{a(b \quad x)}, (a > b)$ when both reactants have different concentrations.	$\frac{1}{k[A]_0}$	mol ^{1}Ls ^{1}	Saponification reaction.
*n*th order reaction		$kt = \frac{1}{n \quad 1}\frac{1}{[A]_t^{n \quad 1}} \quad \frac{1}{[A]_0^{n \quad 1}}$ $n \quad 1$ (First order), where '*n*' is order of the reaction	$\frac{2^{n \quad 1} \quad 1}{k(n \quad 1)[A]_0^{n \quad 1}}$ $n \quad 1$	(mol $L^{1})^{1 \quad n}s^{1}$	

Note Here, $[A]_0$ and $[A]_t$ are the concentrations of reactant at initially and after time, *t* respectively.

Pseudo First Order Reaction

If the concentration of one of the reactant in a second order reaction remains constant because it was supplied in a large excess, its concentration can be neglected from the rate law equation. Hence, the obtaining reaction is known as pseudo first order reaction.

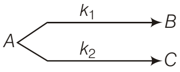
e.g. $r = k[A][B]$

If $[B]$ in large excess, $r = k\ [A]$

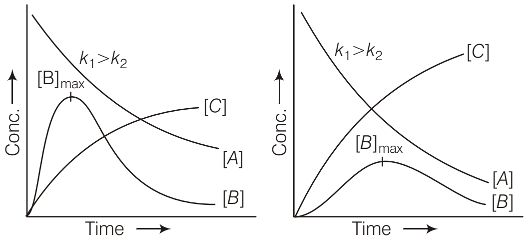
Parallel First Order Reaction

Rate constant $(k) = k_1 + k_2$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$



Consecutive First Order Reaction



Reversible reactions (First order opposed by first order)

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

At $t = 0$, $[A]_0 \quad 0$

At time t, $[A]_0{}^{x} \quad x$

At equilibrium, $[A]_0 \quad x_{eq}\ x_{eq}$

Rate of reaction = Rate of forward reaction Rate of backward reaction

Formulae Related to Parallel, Consecutive and Reversible First Order Reactions

Parallel first order $\frac{d[B]}{dt} = k_1\,[A], \frac{d[C]}{dt} = k_2\,[A],$

$$\frac{d(A)}{dt} = k[A]$$

At any instant: $\frac{[B]}{[C]} = \frac{k_1}{k_2}$

Consecutive first order $\frac{d[B]}{dt} = k_1[A] \quad k_2[B]$

$$[B] = \frac{k_1[A]_0}{k_2 \quad k_1}[e^{\ k_1 t} \quad e^{\ k_2 t}]$$

$$t_{\max} = \frac{2.303}{k_2 \quad k_1}\log\frac{k_2}{k_1}$$

$$[B]_{\max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 \quad k_2}}$$

where, $[A]_0$ = Initial concentration of A
$[B]_{\max}$ = Maximum concentration of B
$t_{\max}$ = Time in which $[B]_{\max}$ converts into C

Reversible reactions $\frac{dx}{dt} = k_f\ [[A]_0 \quad x] \quad k_b x = \frac{k_f\,[A]_0}{x_{eq}}[x_{eq} \quad x]$

$$x_{eq} = \frac{k_f\,[A]_0}{[k_f + k_b]}$$

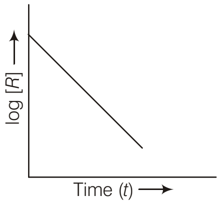
$$(k_f + k_b)t = \ln\frac{x_{eq}}{x_{eq} \quad x}$$

Equilibrium constant $K_c = \frac{[B_{eq}]}{[A_{eq}]} = \frac{K_f}{K_b}$

Best Practice SHOTS

11. For a reaction, graph between logarithm of concentration of reactant *versus* time (t) is given below.

The order and slope for this reaction are respectively



(a) 1st and $\frac{k}{2.303}$
(b) 1st and $\frac{2.303}{k}$
(c) 1st and + $\frac{k}{2.303}$
(d) 1st and + $\frac{2.303}{k}$

12. The rate constant for first order reaction is $5.78 \quad 10^{5}\ \text{s}^{1}$. Percentage of initial concentration of reactant which reacts in 10 h is

[Given, antilog of 0.9031 = 8]

(a) 75% (b) 66.66% (c) 87.5% (d) 50%

13. Consider the following data for the decomposition of ammonium nitrite in aqueous solution.

Volume of N_2 in cc	Time (min)
6.25	10
9.00	15
11.40	20
13.65	25
35.05	infinity

The order of the reaction is

(a) zero (b) one (c) two (d) three

14. Diazonium salt decomposes as

$$C_6H_6N_2^+Cl \longrightarrow C_6H_5Cl + N_2$$

At 0°C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is

(a) a first order reaction
(b) a second order reaction
(c) independent of the initial concentration
(d) a zero order reaction

15. Which of the following reactions is a first order reaction?

(a) NH_2NO_2 ¾ $N_2 + 2H_2O$ *(b)* 2HI ¾ $H_2 + I_2$
(c) $2NO_2$ ¾ $2NO + O_2$ *(d)* $2NO + O_2$ ¾ $2NO_2$

16. For a first order reaction, A B, $k = 5$ min ^{1}. In another first order reaction, C D, only 10% of C decomposes in the time that is required for A to be 50% decomposed. The rate constant for second reaction is

(a) 16.61 $\log_{10}$ 1.11 *(b)* 1.6 $\log_{10}$ 11.1
(c) 10.076 *(d)* 10

17. 87.5% of a radioactive substance disintegrates in 40 min. What is the half-life of the substance?

(a) 11.21 min *(b)* 13.21 min *(c)* 13.32 min *(d)* 14.21 min

18. What is the value of decay constant of a compound having half-life time as 2.95 days?

(a) 2.9 $10^{\ 5}$ $s^{\ 1}$ *(b)* 2.9 10^{6} $s^{\ 1}$
(c) 2.7 $10^{\ 6}$ $s^{\ 1}$ *(d)* 3 10^{5} $s^{\ 1}$

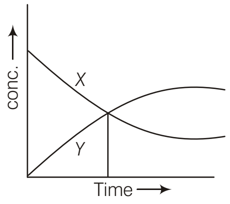
Hint Decay constant, $= \dfrac{0.693}{t_{1/2}}$

19. Hydrolysis of amyl acetate was carried out separately in the presence of 0.02 M HCl and 0.02 M H_2SO_4. The rate constant was found to be k_1 and k_2 respectively. Then,

(a) $k_1 > k_2$ *(b)* $k_2 > k_1$ *(c)* $k_1 = k_2$ *(d)* $k_1 = 2k_2$

Hint Acidic hydrolysis of an ester is a first order reaction,
$r = k$ [ester].
Thus, rate constant does not depends on $[H^+]$. Hence, $k_1 = k_2$.

20. The sidewise graph is shown for change in concentration of species X and Y for the reaction X Y, as function of time. The point of intersection of two curves represents



(a) $t_{1/2}$ *(b)* $t_{1/4}$
(c) $t_{3/4}$ *(d)* $t_{2/3}$

21. The rate law for the reaction $A + 2B$ Product (P) is given by $\dfrac{d[P]}{dt} = K[A]^2 \cdot [B]$, if A is taken in large excess, the order of reaction will be

(a) zero *(b)* 1 *(c)* 2 *(d)* 3

TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION AND COLLISION THEORY OF CHEMICAL REACTIONS

Temperature Dependence of the Rate of a Reaction

The rates of most of the chemical reactions increase as the temperature is raised. The rate constant (k), changes with temperature (T) and it determines the way in which the rate of reaction varies with temperature. This behaviour is summarised by **Arrhenius equation** $k = Ae^{\ E_a/RT}$

where, A = Pre-exponential factor or frequency factor
E_a = Activation energy, R = Gas constant

Activation Energy

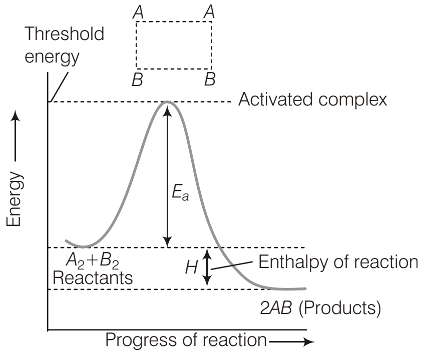
It is defined as the minimum amount of energy required by the reactant molecules to take part in a chemical reaction.

- Lower the activation energy, faster is the reaction, and larger is the value of k.
- Activation energy is always positive, whether the reaction is exothermic or endothermic.
- A positive catalyst decreases E_a value and increases rate of a reaction, whereas a negative catalyst increases E_a value and decreases rate of a reaction.

Note Catalyst neither alter the Gibbs free energy change (G) nor enthalpy change (H) of the reaction. It provides an alternate pathway by altering the potential energy barrier.

Activated Complex Theory

According to Arrhenius, when a reaction takes place, reactant molecules first form an unstable intermediate (activated complex). This intermediate exist for a very short time and breaks up to form products.

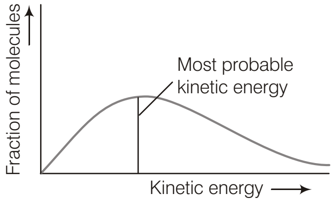


Collision Theory of Chemical Reactions

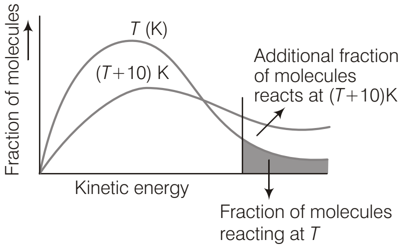
(Temperature Dependence of Rate of Reaction)

Most Probable Kinetic Energy

Maxwell and Boltzmann used statistics for predicting behaviour of large number of molecules in a reaction. According to them most probable kinetic energy is the energy possessed by large fraction of molecules.



Often rate of a reaction increases by a factor of two for a 10 K rise in temperature.



Collision Theory of Bimolecular Gaseous Reactions

This theory is based on kinetic theory of gases.

The main postulates of this theory as follows:

- The reaction between the molecules occurs only when they collide with each other in proper orientations.
- Only those collisions result into chemical reaction in which the molecules acquire energy greater than the activation energy.
- For an effective collision, the colliding molecules must possess threshold energy.
- An activation energy is supplied to the molecules for attaining the threshold energy. During collisions, this energy is acquired by the molecules as a result of interchanges of energies.

Formulae Related to Activation Energy and Collision Theory

- E_a = Threshold energy – average energy of reactants.
- **Effect of temperature on rate of reaction**,

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303RT}\left(\frac{1}{T_1} \quad \frac{1}{T_2}\right), (T_2 > T_1)$$

where, k_1 and k_2 are rate constants at temperatures T_1 and T_2 respectively.

- **Rate of reaction in terms of collision frequency**

$$\text{Rate} = Z_{AB}e^{\;E_a/RT}$$

where, Z_{AB} = collision frequency of reactants A and B

$e^{\;E_a/RT}$ = Fraction of molecules having energy either equal to or greater than E_a.

- For effective collisions,

$$\text{Rate} = pZ_{AB}\,e^{\;E_a/RT}$$

where, p = Steric factor

Best Practice SHOTS

22. For an endothermic reaction, minimum value of activation energy (E_a) will be

(a) less than H
(b) more than H
(c) $H = E_a$
(d) $E_a = 0$

23. For a first order reaction, energy of activation at 25°C without using catalyst is 350 kJ mol ^{1} and with the use of catalyst is 162 kJ mol ^{1}. The ratio of rate constants with the catalyst and to that of without catalyst is

(a) antilog of 23.59
(b) antilog of 23.95
(c) antilog of 32.95
(d) antilog of 32.59

24. Rate constant for the first order decomposition of H_2O_2 is given by the equation,

$\log k = 14.34 \quad 1.25 \quad 10^4/T$, value of activation energy (E_a) for this equation is (in kJ /mol)

(a) 932.43
(b) 392.34
(c) 239.34
(d) 293.43

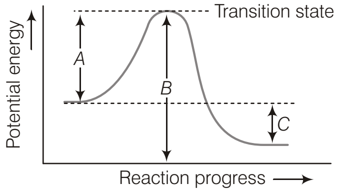
Hint $\because \log k = \log A \quad \dfrac{E_a}{2.303RT}$ ...(i)

$\log k = 14.34 \quad \dfrac{1.25 \quad 10^4}{T}$ ...(ii)

25. With respect to equation, $k = Ae^{\;E_a/RT}$ of chemical kinetics, which one of the following option is correct?

(a) K is equilibrium constant
(b) A is adsorption factor
(c) E_a is energy of activation
(d) R is Rydberg constant

26. Consider the following graph for the reaction $R \quad P$.



$H°$ of the reaction corresponds to the energy

(a) B
(b) A
(c) $B \quad A$
(d) C

27. The formation of H_2O_2 in the upper atmosphere follow the mechanism:

$$H_2O + [O] \;¾\; 2\bar{O}H \;¾\; H_2O_2$$

Given, $H = 72$ kJ mol ^{1}, $E_a = 77$ kJ mol ^{1}

E_a for backward reaction is (in kJ mol ^{1})

(a) 149
(b) 149
(c) 5
(d) 5

28. Collision theory is applicable to

(a) first order reaction
(b) zero order reaction
(c) bimolecular reaction
(d) intermolecular reaction

29. If activation energy (E_a) for the reaction,

$2HI\,(g)$ ¾ $H_2\,(g) + I_2\,(g)$ is 209.5 kJ mol^{1} at 581K. The fraction of molecules of reactant having energy equal to or greater than activation energy is

(a) $4.471 \quad 10^{29}$ *(b)* $1.471 \quad 10^{9}$

(c) $1.21 \quad 10^{5}$ *(d)* antilog of $\overline{19}.1676$

Hint $\log x = \dfrac{E_a}{2.303\,RT}$, where, x = fraction of molecules having energy equal to or more than activation energy.

30. Activation energy for the reaction,

$N_2O_4 \rightleftharpoons 2NO_2$ is E_{a_1}, activation energy E_{a_2} for the reaction, $2N_2O_4 \rightleftharpoons 4NO_2$ is

(a) $E_{a_1} = 2E_{a_2}$ *(b)* $E_{a_2} = 2E_{a_1}$

(c) $E_{a_1} = E_{a_2}$ *(d)* $E_{a_2} = (E_{a_1})^2$

Hint Activation energy does not depend on stoichiometry for a given reaction. Thus, remains same, it is a characteristic property (value) for a particular reaction.

31. A reaction of decomposition is carried out by first order reaction. At 300 K, the decomposition completes 50%, in 20 min. At 350 K, the same substance decomposes 50% in 5 min. The activation energy (E_a)for the reaction is (in kJ mol^{1})

(a) 24.19 *(b)* 75.79 *(c)* 50.07 *(c)* 100.7

Answers

1. (a) **2.** (a) **3.** (c) **4.** (a) **5.** (a) **6.** (b) **7.** (b) **8.** (d) **9.** (d) **10.** (a)
11. (a) **12.** (c) **13.** (b) **14.** (a) **15.** (a) **16.** (a) **17.** (c) **18.** (c) **19.** (c) **20.** (a)
21. (b) **22.** (b) **23.** (c) **24.** (c) **25.** (c) **26.** (d) **27.** (d) **28.** (c) **29.** (d) **30.** (c)
31. (a)

MASTER STROKE

1. The activation energies of two reactions are E_1 and E_2, ($E_1 > E_2$). If the temperature changes from T_1 to T_2, the rate constant of the reactions changes from k_1 to $k_{\ 1}$ in the first reaction and k_2 to k_2 in the second reaction. Predict which of the following expression is correct?

(a) $\dfrac{k_1}{k_1} = \dfrac{k_2}{k_2}$ *(b)* $\dfrac{k_1}{k_1} > \dfrac{k_2}{k_2}$ *(c)* $\dfrac{k_1}{k_1} < \dfrac{k_2}{k_2}$ *(d)* $\dfrac{k_1}{k_1} = \dfrac{k_2}{k_2} = 1$

2. A gaseous reaction, A ¾ $B + 2C$ has specific reaction rate$10^{\ 4}$, when the reaction was complete, the pressure was 750 mm. Calculate the rate of reaction at the initial stage.

(a) 1.5 mm s^{1} *(b)* 2.5 mm s^{1} *(c)* 3.5 mm s^{1} *(d)* 0.5 mm s^{1}

Hint Since, 1 mole of a reactant gives 3 moles of product having the pressure of 750 mm, the initial pressure was 750/3 = 250 mm

$$\frac{dp_A}{dt} = K_p = 10^{\ 2} \quad 250 = 2.5\ \text{mm s}^{\ 1}$$

3. For a reaction $A_2 + B_2$ ¾ $2AB$ the following mechanism is followed.

$$A_2 \overset{k_1}{\rightleftharpoons} A + A\,(\text{fast}), \quad A + B_2 \ \overset{k_2}{¾}\ AB + B\,(\text{slow})$$

$$A + B \ \overset{k_3}{¾}\ AB\,(\text{fast})$$

The order of overall reaction is

(a) 0 *(b)* 1 *(c)* $1\frac{1}{2}$ *(d)* 2

Hint From $A_2 \rightleftharpoons A + A;\quad k_1 = \dfrac{[A]\times[A]}{[A_2]}$ …(i)

$\because$ In main reaction $[A]$ is not present in products thus to eleminate $[A]$,

$[A]^2 = k_1[A_2]$ and $[A] = k_1^{1/2} \times [A_2]^{1/2}$ [From eq. (i)]

From slow step, $r = k_2[A]\times[B_2] = k_2 k_1^{1/2} \times [A_2]^{1/2} \times [B_2]$

Let $k_2 \times k_1 = k, \quad r = k \times [A_2]^{1/2} \times [B_2]$

Hence, order $= 1 + \dfrac{1}{2} = 1\dfrac{1}{2}$

4. Correct order for first order reaction is

(a) $T_{50} < T_{av} < T_{75}$ *(b)* $T_{av} < T_{75} < T_{50}$

(c) $T_{75} < T_{av} < T_{50}$ *(d)* $T_{50} < T_{75} < T_{av}$

Hint $\because T_{av} = 1.44 \quad T_{50}$, i.e. $T_{50} = 0.693 \quad T_{av}$ and $T_{75} = 1.5 \quad T_{50}$

Thus, $T_{50} < T_{av} < T_{75}$

5. If I is the intensity of absorbed light and C, is the concentration of AB for a photochemical reaction, $AB + h$ ¾ $(AB)^*$, the rate of formation of AB^* is directly proportional to

(a) C *(b)* CI *(c)* I *(d)* I^2

Hint Rate of reaction for a photochemical reaction depends on intensity of light (I) and concentration of reactant.

Thus, answer is Þ CI.

6. The decomposition of NH_3 follows rate expression,

$$\text{Rate} = \frac{k_1[NH_3]}{1 + k_2[NH_3]},$$

Above expression behaves as first order reaction, when concentration of NH_3 is

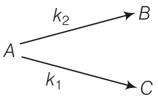
(a) very high *(b)* very low

(c) constant *(d)* can not be predicted

Hint At very low concentration of $[NH_3]\ 1 + k_2\,[NH_3] \quad 1$

Thus, rate $= k_1[NH_3]$

7. A substance decomposes via two parallel first order reactions. The rate constants for these reactions are given as



$k_1 = 1.26 \quad 10^{\ 4}\,s^{\ 1}$, $k_2 = 3.8 \quad 10^{\ 5}\,s^{\ 1}$

The percentage distribution of B and C are

(a) 75% of B and 25% of C *(b)* 66.66% of B and 33.33% C

(c) 76.83% of B and 23.17% of C *(d)* 80% of B and 20% of C

Hint For first order decomposition,

$$\frac{\text{Rate of formation of } B}{\text{Rate of formation of } C} = \frac{1.26 \times 10^{-4}}{3.8 \times 10^{-5}} = \frac{12.6 \times 10^{-5}}{3.8 \times 10^{-5}}$$

$$\frac{[B]}{[C]} = \frac{12.6}{3.8} = \frac{126}{38}$$ and total concentration = 126 + 38 = 164

Thus, (i) % of $B = \frac{126}{164} \times 100 = 76.83\%$

(ii) % of $C = 100 - 76.83 = 23.17\%$

8. The rate law for a reaction is $r = k\,[A]^n[B]^m$, on doubling the concentration of A and halving the concentration of B, the ratio of new rate to the earlier rate of reaction will be

(a) $(m + n)$ (b) $\frac{1}{2^{m+n}}$
(c) 2^{n-m} (d) $(n - m)$

9. In the reaction, $xA + yB \longrightarrow$ Products,
when concentrations of both the reactants A and B are doubled, the rate increased by eight times. But when concentration of A is doubled keeping concentration of B constant, the rate of reaction increased by two times.
The order of reaction is

(a) 0 (b) 1
(c) 2 (d) 3

10. For the reaction, $A(g) + 2B(g) \longrightarrow 2C(g)$ using the following results. The rate law will be

Exp. no.	Initial conc. of $[A]$ mol L^{-1}	Initial conc. of $[B]$ mol L^{-1}	Initial rate of formation of $[C]$, mol L^{-1}
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

(a) $r = k[A]^2[B]^2$ (b) $r = k[A][B]$
(c) $r = k[A]^2[B]$ (d) $r = k[A][B]^2$

Hint ∵ Rate $\propto$ [conc.]^n, from exp. no.(1) and (2)
rate $\propto [B]^n$ (keeping A constant)
$4 \propto [B]^n$ (n = order of reaction with respect to B)
$n = 2$, i.e. order of of reaction with respect to $B = 2$.

11. For the following reaction,

$$\text{Cl}_2(aq) + \text{H}_2\text{S}(aq) \longrightarrow \text{S}(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq)$$

the rate equation is $r = k[\text{Cl}_2][\text{H}_2\text{S}]$

The two possible mechanisms of the above reaction are

I. (i) $\text{Cl}_2 + \text{H}_2\text{S} \xrightarrow{\text{Slow}} \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^-$
(ii) $\text{Cl}_2 + \text{H}^+ + \text{HS}^- \xrightarrow{\text{Fast}} \text{H}^+ + \text{Cl}^- + \text{S}$

II. $\text{H}_2\text{S} \xrightleftharpoons{\text{Fast}} \text{H}^+ + \text{HS}^-$
$\text{Cl}_2 + \text{HS}^- \xrightarrow{\text{Slow}} 2\text{Cl}^- + \text{H}^+ + \text{S}$

Which of these mechanism is/are consistent with the given rate equation?

(a) Only I (b) Only II
(c) I and II (d) None of these

Hint Slowest step will be the rate determining step, thus in
case I, rate $= r = k \cdot [\text{Cl}_2][\text{H}_2\text{S}]$ and
in case II, rate $= r = k \cdot [\text{Cl}_2][\text{HS}^-][\text{H}^+]$
Hence, only mechanism I is consist for the given rate law.

12. For the reaction, $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of A is related to rate of appearance of B by the expression.

(a) $-\frac{d}{dt}[A] = \frac{1}{2}\frac{d}{dt}[B]$
(b) $-\frac{d}{dt}[A] = 4\frac{d}{dt}[B]$
(c) $-\frac{d}{dt}[A] = \frac{1}{4}\frac{d}{dt}[B]$
(d) $-\frac{d}{dt}[A] = \frac{d}{dt}[B]$

13. A radioactive element fallen over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times of the permissible value, after how many days will it be safe to enter the room?

(a) 1000 days (b) 500 days
(c) 300 days (d) 100 days

Hint ∵ Activity $\propto N$ (quantity)

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n \quad (\because n = \text{number of half-lifes})$$

14. If n_t is the number of radioactive atoms present at time t, then for the first order reaction, which of the following will be constant?

(a) $\frac{n_t}{t}$ (b) $\log_e \frac{n_t}{t}$
(c) $\frac{d}{dt}[\log_e \cdot n_t]$ (d) n_t

Hint ∵ Rate $= -\frac{dn_t}{dt} = \lambda \cdot n_t \Rightarrow \frac{dn_t}{n_t \cdot dt} = -\lambda$

$\Rightarrow \frac{d}{dt}(\log_e n_t) = -\lambda$ (constant)

15. Variation of rate constant with the temperature is given by $\log_{10} k = -\frac{E_a}{2.303RT} + \text{constant}$

If for a certain reaction, $\log_{10} k = -\frac{3153}{T} + 11.890$

The value of activation energy is (in kJ mol^{-1})

(a) 20.48 (b) 40.48 (c) 50.37 (d) 60.37

Answers

1. (b)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (b)	**6.** (b)	**7.** (c)	**8.** (c)	**9.** (d)	**10.** (d)
11. (a)	**12.** (c)	**13.** (d)	**14.** (c)	**15.** (d)					

Metallurgy

EXTRACTION AND ISOLATION OF ELEMENTS

Metals occur in two forms in nature

(i) In native state

(ii) In combined state

Less reactive metals (Ag, Au, Pt etc.) are found in native state (free state) and are not attacked by O_2, H_2O and CO_2 while reactive metals (Na, Ca, Mg etc.) are found in combined state in nature and attacked by O_2, H_2O and CO_2.

Ore An ore is a complex mixture of a metal-containing mineral and economically worth less material called gangue, consisting of sand, clay and other impurities.

Steps Involving Extraction of Metals

Step **1** Concentration of ore and, if necessary, chemical treatment prior to the reduction.

Step **2** Reduction of the mineral to the free metal.

Step **3** Refining or purification of metal.

Common ores of some important metals

Metals	Ore	Formula
Li	Spodumene	$LiAlSi_2O_6$
	Lepidolite	$(Li, Na, K)_2Al_2(SiO_2)_3F(OH)$
Na	Common salt	NaCl (rock salt)
	Chile salt petre	$NaNO_3$
	Glauberite	$Na_2SO_4 \cdot 10H_2O$ (Glauber's salt)
	Borax	$Na_2B_4O_7 \cdot 10H_2O$
	Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
	Soda ash	Na_2CO_3
	Feldspar	$NaAlSi_3O_8$
K	Sylvine	KCl
	Nitre	KNO_3 (saltpeter)
	Schonite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
Mg	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3 \cdot CaCO_3$
	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
	Epsom salt	$MgSO_4 \cdot 7H_2O$
Ca	Gypsum	$CaSO_4 \cdot 2H_2O$
	Limestone	$CaCO_3$
	Phosphorite	$Ca_3(PO_4)_2$
	Fluorspar	CaF_2
Al	Bauxite	$Al_2O_3 \cdot 2H_2O$
	Diaspore	$Al_2O_3 \cdot H_2O$
	Corundum	Al_2O_3
	Cryolite	Na_3AlF_6
Sn	Cassiterite	SnO_2 (tin stone)
Pb	Galena	PbS
	Cerussite	$PbCO_3$
	Anglesite	$PbSO_4$
Cu	Chalcopyrite	$CuFeS_2$ (copper pyrite)
	Chalcocite	Cu_2S (copper glance)
	Cuperite	Cu_2O
	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
Ag	Argentite	Ag_2S (silver glance)
	Cerargyrite	AgCl (horn silver)
	Pyrargyrite	$Ag_2S \cdot Sb_2S_3$ (Ruby silver)
Fe	Haematite	Fe_2O_3
	Limonite	$Fe_2O_3 \cdot 3H_2O$
	Magnetite (lodestone)	Fe_3O_4 (magnetic oxide of iron)
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
Hg	Cinnabar	HgS
Zn	Zinc blende	ZnS (black zinc or sphalerite)
	Calamine	$ZnCO_3$
	Zincite	ZnO (red zinc)
Mn	Pyrolusite	MnO_2
	Manganite	$Mn_2O_3 \cdot H_2O$
Cr	Chromite	$Cr_2O_3 \cdot FeO$

Crushing of Ore

Crushing and grinding of ores are done in order to ease the process of concentration of ores. They are crushed into small pieces in gyratory crushers followed by grinding.

Concentration of Ores

It involves the removal of unwanted materials like sand, clays, etc., from the ore. The procedure followed depends on physical properties of compounds of minerals and impurities present in it.

Some of the important methods involved are:

Gravity Separation or Levigation

It is based on difference in the density of the ores and the gangue particles. The powdered ore is washed in a running stream of water. The lighter gangue particles are washed away leaving the heavier ores. Fe_2O_3, Fe_3O_4, etc., are concentrated by this method.

Froth Floatation Method

Sulphide ores of Cu, Ag, Zn, Pb, etc., are concentrated by this process.

- A suspension of powdered ore in water is made followed by the addition of collectors (pine oil, fatty acids, xanthates, etc.) and froth stabilisers (cresol, aniline, etc.).
- Ore particles are made wet by oil and come to surface as froth, whereas gangue particles remain inside with water.

Magnetic Separation Method

It is based on difference in magnetic properties of gangue and ores. The ore is concentrated by a magnetic separator, that separates magnetic substances from non-magnetic substances. Magnetite (Fe_3O_4), chromite ($FeO \cdot Cr_2O_3$), pyrolusite (MnO_2), tungsten ore, etc., are separated by this method.

Leaching

In this process, the ore is made soluble in a suitable solvent leaving the insoluble gangue particles behind. The ore is then recovered from the solution by suitable chemical method.

Leaching of Bauxite

$$\underset{\substack{\text{Bauxite} \\ \text{Ore with impurity}}}{(Al_2O_3)} \xrightarrow[\text{High temperature and pressure}]{\text{Conc. NaOH}}$$

$$Na[Al(OH)_4](aq) \xrightarrow{CO_2(g)} Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470\text{ K}} \underset{\text{Pure form}}{Al_2O_3(s)}$$

Leaching of Ag and Au Ores

Ag and Au ores are concentrated as metal cyanide by treating them with dilute NaCN or KCN, from which pure metal is obtained by replacement reaction.

EXTRACTION OF CRUDE METAL FROM CONCENTRATED ORE

Highly Active Metals (e.g. Na, K, Mg etc.)

Electrolytic Reduction The oxides of highly electropositive metals do not reduce easily with coke. Hence, they are extracted by electrolysis of their salts in fused sate. Pure metal is obtained at cathode.

Less Active Metals

Roasting Sulphide ores are converted to oxide ores by roasting. The ore is treated in a furnace in regular supply of air at a temperature below the melting point of the metal. The sulphide ores are converted to metal oxides and the impurities are removed as volatile oxides.

Calcination Hydroxide and carbonate ores do not undergo roasting, hence they are heated below melting point in absence of air forming metal oxides.

Metal Oxide

Reduction of Oxide to Metal Metal oxides are reduced to the corresponding metals by various processes based on standard reduction potential called pyrometallurgical process and hydrometallurgical process.

Impure Metal

Refining of Impure Metal The impure metal obtained from the reduction of metal oxide contains impurities that are refined to get pure metal.

Pure Metal

Various processes for reduction of metal oxides to metal are given below

Smelting The concentrated ore is treated with coke and flux and heated at high temperature and the process is called smelting. The coke reduces metal oxide to metal and flux removes acidic or basic impurities as slag :

With Hydrogen $MO_3 + 3H_2 \longrightarrow M + H_2O \quad (M = \text{Mo or W})$

Goldschmidt Aluminothermic Process Cr and Mn oxides are reduced by this process.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

With Other Metals Highly active metals reduce less active metal oxides.

$$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$$

Self Reduction or Auto-reduction A part of sulphide ore of less electropositive metals like Hg, Pb, Cu, etc., are converted to oxide ore. The sulphide and oxide ores undergo self-reduction to form the metal.

e.g. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2(g)$

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2(g)\uparrow$

Note **Pyrometallurgy** In this process metal is extracted by heating metal oxide with a suitable reducing agent.

Hydrometallurgy In this process metal is extracted by dissolving the ore in a suitable reagent followed by precipitation of metal by a more electropositive metal.

Rock Music and Metallurgy

- Metallurgy plays a big role in rock music, without it rock music as we know would not exist.
- The strings of the guitar being played are the product of complex technology.
- The core of the strings is made of mild steel, varying in hardness and ductility, depending on the type of guitar on which it will be used.
- The core string is wound with fine wrap wire, composed typically an alloy of copper and zinc for acoustic guitar use, or stainless steel for electric guitars.
- Artists can be very passionate about the particular makes and models of strings they use.

Best Practice SHOTS

1. Which of the following metal has the largest abundance in the earth's crust?

(a) Aluminium
(b) Calcium
(c) Magnesium
(d) Sodium

2. Sulphides ores are common for the metals

(a) Ag, Cu and Pb
(b) Ag, Cu and Sn
(c) Ag, Mg and Pb
(d) Al, Cu and Pb

3. Smelting involves reduction of metal oxide with

(a) carbon (b) carbon monoxide
(c) magnesium (d) aluminium

4. During smelting, an additional substance is added which combines with impurities to form a fusible mass. The additional substance is called

(a) flux (b) slag (c) gangue (d) ore

5. Which of the following metals are found in native state?

(a) Ag, Pb and Fe (b) Ag, Pt and Mg
(c) Au, Pt and Ag (d) Cu, Al and Zn

6. The ore having two different metal atoms is

(a) haematite (b) galena
(c) magnetite (d) copper pyrites

Hint (d) $CuFeS_2$ (Cu and Fe)

7. The salt which is least likely to be found in minerals is

(a) chloride (b) sulphate (c) sulphide (d) nitrite

Hint (d) Nitrite salt which is least likely to be found in minerals because all nitrates are soluble in water.

8. Which of the following benefication process is used for the minerals, $Al_2O_3 \cdot 2H_2O$?

(a) Froth floatation (b) Leaching
(c) Liquation (d) Magnetic separation

Hint (b) Leaching process is used for the minerals $Al_2O_3 \cdot 2H_2O$.

9. Heating pyrite to remove sulphur is called

(a) smelting (b) calcination (c) liquation (d) roasting

Hint (d) Heating pyrite to remove sulphur is called roasting.

10. In the extraction of metal M from its sulphide ore is formed by reduction with Cu_2O is

(a) Fe (b) Co (c) Cu (d) Zn

THERMODYNAMICS AND ELECTROCHEMICAL PRINCIPLES OF METALLURGY

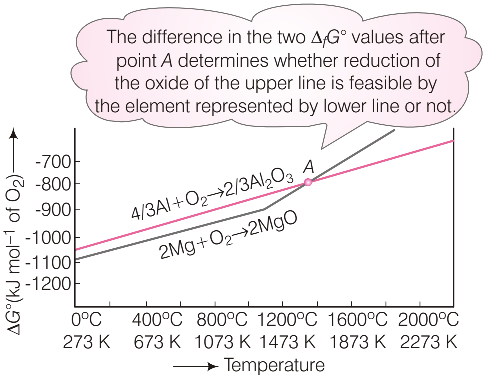
Thermodynamics of Metallurgy

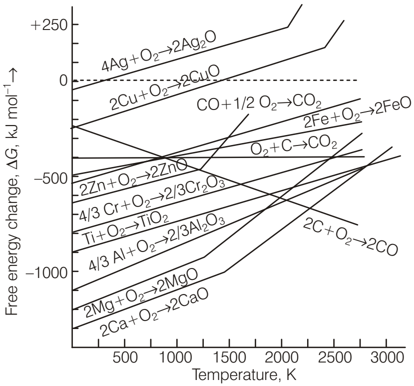
For a reaction to be spontaneous, $\Delta_f G°$ value should be negative. Hence, during the reduction of metal oxides, a reducing agent with a negative value of $\Delta_f G°$ that is sufficient to make the over all $\Delta_f G°$ value negative.

Ellingham Diagram

It represents $\Delta_f G°$ *versus* temperature for the formation of oxides of elements.

- Each plot is a straight line except when a phase change occurs.
- There is a point in the curve below which $\Delta_f G°$ is negative (the oxide is stable) and above this point the metal oxide is decomposed to form metal.
- This diagram is useful in choosing a reducing agent for the reduction of metal oxides.


The difference in the two $\Delta_f G°$ values after point A determines whether reduction of the oxide of the upper line is feasible by the element represented by lower line or not.



Combined Ellingham diagram for metal and carbon

Limitations of Ellingham Diagram

(i) These do not explain the kinetics of reduction processes.
(ii) It is assumed that system is always in the state of equilibrium, which is not true.

Steeling of Automobiles

- Steel (many iron alloys are collectively known as steels) is the most recycled consumer product, given that about 95% of steel from automobiles is recycled.
- The steel recycling institute estimates that 14 million tons of steel scrap from automobiles was recycled in the year 2000.
- Approximately 14×10^6 tons of iron (steel) is recycled. Each 10^3 tons iron ore contains 20 tons Fe_3O_4 is which there are 168 tons Fe per 232 tons Fe_3O_4.
- About 1×10^9 tons of ore did not have to be mined because of using recycled steel, saving a substantial amount of material and the energy needed to process the ore.

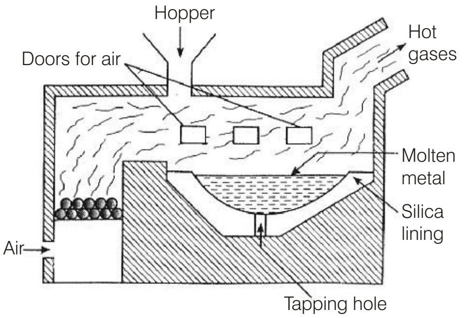
Furnaces

It is a device in which high temperature is produced either by burning fuel or by using electricity. Several type of furnaces are used in the metallurgy. Some important ores among them are:

Reverberatory Furnace

This is made up of fire bricks containing fire place, hearth and chimney. The ore is not directly heated in this furnace.

The fuel gas doesn't come in direct contact with the material, hence can be used for both oxidation and reduction. If reduction is required, the ore is mixed with some reducing agent while oxidation is required, hot air blown in it. It is used for extraction of Cu, Pb, Sn, etc.

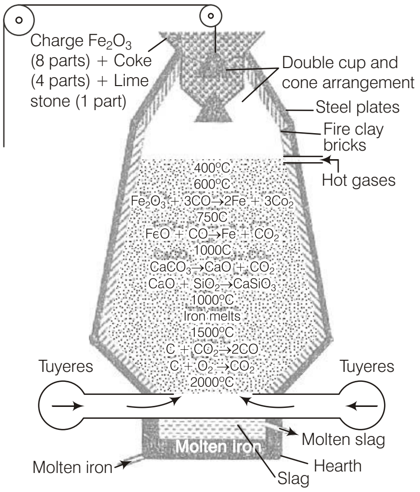


Reverberatory furnace

Blast Furnace

This is a steel structure lined with fire bricks. It is narrow at both the top and bottom, but wider at middle.

There is a hopper at the top through which concentrated ore, coke and flux are inserted. There are different temperature zones in the furnace where different reactions take place. The molten metal is obtained at the bottom. Fe, Cu, Pb, etc., are purified in the furnace.

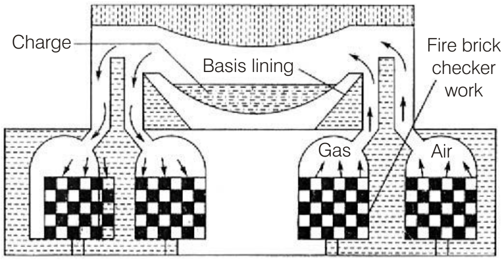


Metallurgy of Fe : Reactions inside a blast furnace

Siemens Martin Open Hearth Furnace

Used in the manufacture of steel. The furnace is lined with CaO and MgO.

- A mixture of molten cast iron, Fe_2O_3 and $CaCO_3$ is heated by producer gas. The impurities are oxidised and removed.
- The molten iron is mined with required amount of spiegel (an alloy of Fe, C, Mn) to obtain steel of required quality.



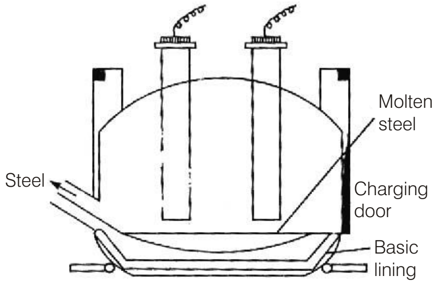
Open hearth process

Advantages of Open Hearth Process

- This process is slower and easier to work.
- Samples can be examined from time to time. Thus, the quality of steel can be controlled.
- Since, heating is done externally, thus, temperature can be controlled more effectively.

Electric Furnaces

In these furnances, electrical energy is converted into heat energy. Such furnace are largely used where cheap power is available and very high temperatures are required and also for carrying electrolytic reduction.



Electric furnace process

Essential Transition Metals in Nutrition

Of the ten trace elements known to be essential to human nutrition, seven are transition metals. For the most part transition metals are present in biochemical compounds as complex ions, chelated by organic ligand for, e.g. haemoglobin has such a structure with Fe^{2+} as the central ion of the complex. The Co^{3+} ion occupies a similar position in vitamin-B_{12}, octahedrally coordinated to organic molecules somewhat similar to those in haemoglobin. Transition metal cations are frequently found in enzymes. The Zn^{2+} ion alone is known to be a component of at least 70 different enzymes.

Although Zn^{2+} is essential to human nutrition, compounds of the two elements below zinc in the periodic table, Cd and Hg are extremely toxic. This reflects the fact that Cd and Hg^{2+}, in contrast to Zn^{2+}, form very stable complexes with ligands containing sulphur atoms. As a result, these two cations react with and thereby deactivate enzymes containing —SH group.

Best Practice SHOTS

11. According to Ellingham diagram, the oxidation reaction of carbon to carbon monoxide may be used to reduce which one of the following oxides at the lowest temperature?

(a) Al_2O_3 (b) Cu_2O (c) MgO (d) ZnO

Hint (b) The graph of $\Delta_f G° \text{ vs } T$ in the Ellingham diagram shows that $Cu - Cu_2O$ line is atmost at the top (i.e. much higher than those of Al - Al_2O_3, Mg-MgO, Zn-ZnO and Fe-FeO) lines. Therefore, Cu_2O can be reduced to Cu at the lowest temperature.

12. Identify the reaction that does not take place in a blast furnace.

(a) $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
(b) $CO_2 + C \longrightarrow 2CO$
(c) $CaCO_3 \longrightarrow CaO + CO_2$
(d) $FeO + SiO_2 \longrightarrow FeSiO_3$

Hint (d) $CaSiO_3$ formation takes place in blast furnance ($FeSiO_3$ is not formed).

$$CaO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

13. Among the metals Cr, Fe, Mn, Ti, Ba and Mg, the one that cannot be obtained by reduction of metal oxide by aluminium is

(a) Cr (b) Fe (c) Mg (d) Ba

Hint (c) Mg metal cannot be obtained by reduction of MgO by aluminium because Mg is more reactive than Al.

14. Iron obtained from blast furnace is

(a) wrought iron (b) cast iron (c) pig iron (d) steel

15. On igniting Fe_2O_3 at 1400°C, the product obtained is

(a) Fe_2O_3 melt (b) FeO (c) Fe_3O_4 (d) metallic iron

16. Heating mixture of Cu_2O and Cu_2S will gave

(a) $Cu + SO_2$ (b) $Cu + SO_3$ (c) $CuO + CuS$ (d) $Cu_2 + SO_3$

Hint $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

Auto reduction takes place

17. $\Delta G°$ *vs* T plot in the Ellingham's diagram slopes downwards for the reaction.

(a) $Mg + \frac{1}{2}O_2 \longrightarrow MgO$ (b) $2Ag + \frac{1}{2}O_2 \longrightarrow Ag_2O$

(c) $C + \frac{1}{2}O_2 \longrightarrow CO$ (d) $CO + \frac{1}{2}O_2 \longrightarrow CO_2$

18. Which of the following reactions, taking place in the blast furnace during extraction of iron is endothermic?

(a) $CaCO_3 \longrightarrow CaO + CO_2$
(b) $2C + O_2 \longrightarrow CO$
(c) $C + O_2 \longrightarrow CO_2$
(d) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

19. Which out of the following reactions, does not indicate slag formation?

(a) $Fe_2O_3 + P_2O_5 \longrightarrow 2FePO_4$
(b) $PbO + SiO_2 \longrightarrow PbSiO_3$
(c) $3MgO + P_2O_5 \longrightarrow Mg_3(PO_4)_2$
(d) None of the above

Hint $FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$

20. Selection of temperature to carry out a reduction process depends so as to make

(a) ΔG negative (b) ΔG positive
(c) ΔH negative (d) ΔH positive

REFINING OF METALS AND EXTRACTION SCHEME OF SOME METALS

Metals extracted through any of the methods described in topic 1 and 2 are usually contain some impurities. Following methods are used to purify the metals.

1. **Distillation Method** Metals with low boiling point like Zn, Cd, Hg, etc., are evaporated to collect the pure metal.
2. **Liquation Method** Metals with low melting point like, Sn, Pb, Hg, Bi, etc., are separated from high melting impurities by this method.
3. **Electrolysis** The impure metal act as anode and deposited at cathode as pure metal. The electrolysis is carried out in a cell containing aqueous solution of the salt of the metal. The more basic impurities remain in solution and less basic impurities are deposited as anode mud, e.g. Cu, Zn, Ag, Au, Al, etc.
4. **Zone-refining Method** This is based on the principle that impurities are more soluble in molten state than in the solid state of metal. The metal obtained is highly pure. The impure metal on gradual cooling deposit as pure crystal of metal leaving impurities in the remaining part of molten metal. Ge, Si, B, Ga, in are purified by this method.
5. **Vapour Phase Refining Method** The impure metal is converted into its volatile compound, which on heating is decomposed to pure metal.

Mond process

$$Ni + CO \xrightarrow{330-350\text{ K}} \underset{\text{Volatile compound}}{Ni(CO)_4}$$

$$Ni(CO)_4 \xrightarrow{450-470\text{ K}} Ni + 4CO$$

van-Arkel Method This method is used to remove oxygen and nitrogen impurities in metals like Zr, Ti, V, Th, etc., e.g.

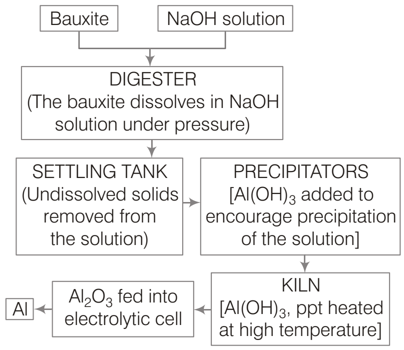
$$Ti + 2I_2 \xrightarrow{150-250°C} \underset{\text{Volatile compound}}{TiI_4(g)}$$

$$TiI_4(g) \xrightarrow[\text{Tungsten filament}]{1400°C} \underset{\text{(Pure)}}{Ti(s)} + 2I_2(g)$$

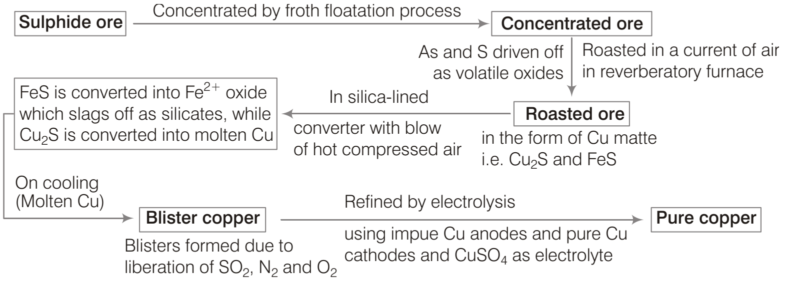
6. **Hydrometallurgical Process** The ore is treated with reagents like NaCN or Cl_2 in presence of water. The metal forms salt solution that is recovered in pure form either by electrolysis or by replacement reaction in the solution.
7. **Amalgamation Process** Noble metals like Ag, Au when come in contact with Hg form amalgam, from which pure metal is obtained by distillation.
8. **Chromatographic Method** This is based on the principle that different compounds of a mixture are differently adsorbed on an adsorbent. This method is used when the impurities are very close in their chemical properties and the metal is present in very minute quantity.
9. **Poling Method** The impure metal containing oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. This pole release hydrocarbon gases which reduce the oxide impurities. This method is used specially in case of copper.
10. **Cupellation** In this process ores or alloyed metals are treated under very high temperatures and have controlled operations to separate noble metals like Ag and Au, from base metals like Zn, Bi, As etc. This method is known as cupellation because impure metal is fused in small boat shaped dishes of bone ash or cement called carpels.
11. **Bessemerisation** In this process, the impure metal is heated in Bessemer converter and a blast of compressed air is blown through the molten mass. The impurities get removed in the form of volatile oxides. This process is used in making steel from cast iron, in purification of Ni etc.

Extraction Scheme of Some Important Metals

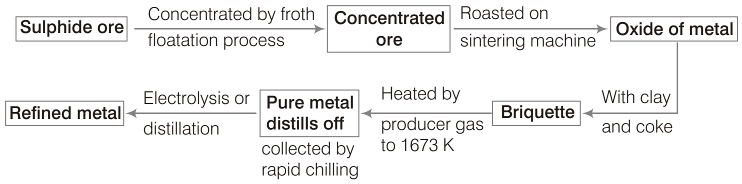
Aluminium



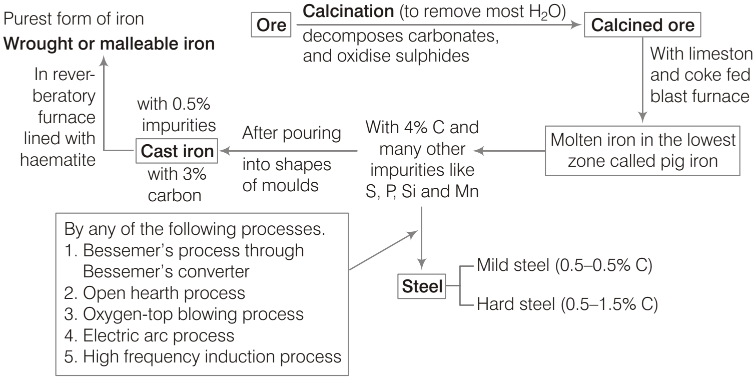
Copper



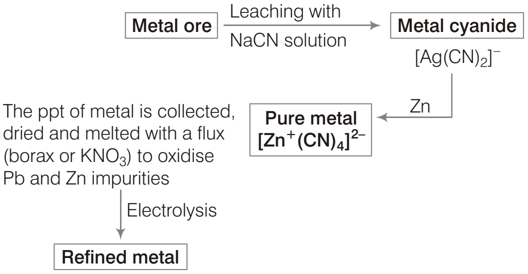
Zinc



Iron

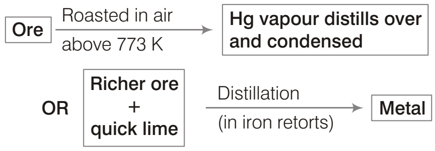


Silver



Mercury

It is found as 1×10^{-5}% of earth crust and its most important ore is cinnabar (HgS).



Purification It can be purified by dropping slowly through dil. HNO_3. The metallic impurities displace Hg from nitrate and go into the solution. Further purification is carried out by distillation under reduced pressure.

Best Practice SHOTS

21. Calcium is obtained by the
(a) roasting of lime stone
(b) electrolysis of solution of calcium chloride in H_2O
(c) electrolysis of molten anhydrous calcium chloride
(d) reduction of calcium chloride with carbon

22. Blister Cu is about
(a) 60% Cu *(b)* 90% Cu *(c)* 98% Cu *(d)* 100% Cu

Hint *(c)* After bessemerisation of the concentrated ore, Cu obtained is 98 % pure. It is called blister Cu.

23. During electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are
(a) Sn and Ag *(b)* Pb and Zn
(c) Ag and Au *(d)* Fe and Ni

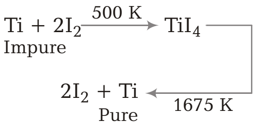
24. Which of the following refining method and crude metals are not correctly matched?
(a) Distillation-Zinc and mercury
(b) Liquation-Tin
(c) van-Arkel-Zirconium
(d) Mond process-Lead

25. The process of isolation of metals by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called
(a) electrometallurgy
(b) hydrometallurgy
(c) electro-refining
(d) zone-refining

26. Vapour phase refining of nickel is carried out using
(a) I_2 *(b)* Cl_2 *(c)* HCl *(d)* CO

27. Which of the following refining method and crude metals are not correctly matched?
(a) Liquation-Tin
(b) Zone refining-Silicon
(c) Mond process-Aluminium
(d) Electrolytic refining-Blister copper

28. Which method of purification is represented by the equations?



(a) Cupellation *(b)* Poling
(c) van-Arkel *(d)* Zone refining

29. Which of the following method is used for obtaining aluminium metal?
(a) Electrolysing fused Al_2O_3 and cryolite
(b) By heating alumina with carbon
(c) By heating alumina in muffle furnace
(d) By a process called pyrometallurgy

30. Poling process
(a) reduced SnO_2 to Sn
(b) oxidised impurities like iron and removes as scum
(c) uses green poles of wood
(d) involves all of the above.

Answers

1. (a) **2.** (a) **3.** (a) **4.** (a) **5.** (c) **6.** (d) **7.** (d) **8.** (b) **9.** (d) **10.** (c)
11. (b) **12.** (d) **13.** (c) **14.** (c) **15.** (d) **16.** (a) **17.** (c) **18.** (d) **19.** (d) **20.** (a)
21. (c) **22.** (c) **23.** (c) **24.** (d) **25.** (b) **26.** (d) **27.** (c) **28.** (c) **29.** (a) **30.** (d)

MASTER STROKE

1. Which one of the following elements constitutes a major impurity in pig iron?
(a) Silicon *(b)* Oxygen
(c) Sulphur *(d)* Carbon

2. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of
(a) nitrogen *(b)* oxygen
(c) carbon dioxide *(d)* argon

Hint *(b)* $4Hg + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$

3. Which step is not involved in hydrometallurgical process?
(a) $Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$
(b) $CuSO_4 + Fe \longrightarrow Cu + FeSO_4$
(c) $CuFeS_2 + 2H_2SO_4 \longrightarrow CuSO_4 + FeSo_4 + 2H_2S$
(d) $CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$

4. Extraction of zinc from zinc blende is achieved by
(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with other metal
(d) roasting followed by self reduction

Hint *(b)* Roasting followed by reduction with carbon.

5. By annealing steel
(a) becomes soft
(b) becomes liquid
(c) becomes hard and brittle
(d) is covered with a thin film of Fe_3O_4

6. In alumino thermite process aluminium acts as
(a) an oxidising agent
(b) a flux
(c) a reducing agent
(d) a solder

7. The methods chiefly used for the extraction of lead and tin from their ores are respectively
(a) self reduction and carbon reduction
(b) self reduction and electrolytic reduction
(c) carbon reduction and self reduction
(d) cynide process and carbon reduction

8. When copper pyrite is roasted in excess of air, a mixture of CuO+FeO is formed. FeO is present as impurity. This can be removed as slag during reduction of CuO. The flux added to form slag is
(a) SiO_2, which is an acidic flux
(b) lime stone, which is basic flux
(c) SiO_2, which is the basic flux
(d) CaO, which is a basic flux

9. Which is chloride ore of Mg?
(a) Kiserite
(b) Carnallite
(c) Epsomite
(d) Dolomite

10. Corundum is ...... mineral of Al.
(a) silicate
(b) oxide
(c) double salt
(d) sulphate

11. Purest form of iron is
(a) cast iron
(b) wrought iron
(c) pig iron
(d) None of these

12. Which of the following is not an ore of a metal?
(a) Malachite
(b) Calamine
(c) Stellite
(d) Cerussite

13. Black tin is
(a) an alloy of Sn
(b) an allotrope of Sn
(c) 60 – 70% SnO_2
(d) 100 % SnO_2

Hint *(c)* 60-70% SnO_2 called black tin.

14. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out
(a) in presence of NaCl
(b) in presence of fluorite
(c) in the presence of cryolite which forms a melt with lower melting temperature
(d) in the presence of cryolite which forms a melt with higher melting temperature

15. $\text{Ag} + \text{Na}_2\text{CO}_3 \longrightarrow \text{Ag}_2\text{CO}_3 \xrightarrow{\Delta} X$
(a) Ag_2O and CO_2
(b) Ag, O_2 and CO_2
(c) Ag_2O_2 and CO_2
(d) No effect

Hint *(b)* $X =$ Ag, O_2 and CO_2

16. In the equation,

$$4M + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\,[M(\text{CN})_2] + 4\text{OH}^-$$

The metal *M* is
(a) copper
(b) iron
(c) gold
(d) zinc

Hint *(c)*

$$\underset{\substack{[M=\text{Au}]\\ \text{Gold}}}{4\text{Au}} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \xrightarrow{O_2} 4\bar{\text{O}}\text{H} + 4[\text{Au(CN)}_2]$$

17. The auto-reduction process is not used in the metallurgy of
(a) Hg
(b) Cu
(c) Pb
(d) Fe

18. In the process of extraction of gold,

$$\text{Roastedgoldore}+\text{CN}+\text{H}^{-}\quad {}_2\text{O} \xrightarrow{O_2} \bar{\text{O}}\text{H}+[\ \ X]$$

$$[X] + \text{Zn} \longrightarrow [Y] + \text{Au}$$

Identify the complexes [*X*] and [*Y*]
(a) $X = [\text{Au(CN)}_2]^-$; $Y = [\text{Zn(CN)}_4]^{2-}$
(b) $X = [\text{Au(CN)}_4]^{2-}$; $Y = [\text{Zn(CN)}_4]^{2-}$
(c) $X = [\text{Au(CN)}_2]^-$; $Y = [\text{Zn(CN)}_6]^{4-}$
(d) $X = [\text{Au(CN)}_4]^-$; $Y = [\text{Zn(CN)}_4]^{2-}$

19. Which of the following is used in thermite welding?
(a) $\text{TiO}_2 + 4\text{Na} \longrightarrow \text{Ti} + 2\text{Na}_2\text{O}$
(b) $2\text{Al} + \text{Fe}_2\text{O}_3 \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
(c) $\text{SnO}_2 + 2\text{C} \longrightarrow \text{Sn} + 2\text{CO}$
(d) $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$

Answers

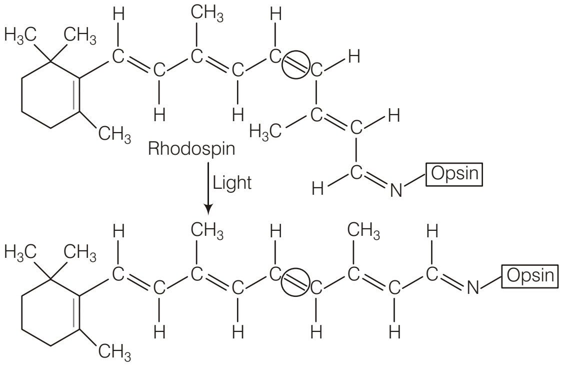
1. (d)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (c)	**7.** (a)	**8.** (a)	**9.** (b)	**10.** (b)
11. (b)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (b)	**16.** (c)	**17.** (d)	**18.** (a)	**19.** (b)	

DO YOU KNOW ?

Do you know, our clear visibility is due to rigidity of double bonds in retinal?

We see things around us, when light is focused by the lens of our eye onto the retina, the layer of cells lining the interior of the eyeball. The retina contains photoreceptor cells called rods and cones. The human retina contains about 3 million cones and 100 million rods. The rods are sensitive to dim light and cones to colours. The tops of the rods and cones contain a molecule called rhodopsin. Rhodopsin consists of a protein called opsin, bonded to a reddish-purple pigment called retinal. Our vision depends on the rigidity of double bonds in retinal.

In its normal form, retinal is held rigid by its double bonds. Light entering the eye is absorbed by rhodopsin and the energy is used to break the π-bond portion of the circled double bond. The molecule then rotates around this bond, changing its geometry. The retinal then separates from the opsin, triggering the reactions that produce a nerve impulse that the brain interprets as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus, only five photons of light are necessary to stimulate the eye.



Do you know, chemical bonds differ only in intensity of electrostatic force of attraction?

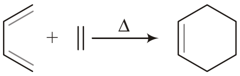
In chemical bonding, we study about different kinds of bonds like, ionic, covalent, coordinate, metallic, hydrogen and van der Waals' bonds. All of these bonds differ from each other only in intensity of electrostatic force of attraction. This attraction occurs between electrons and nucleus, either of same species or of two different species. The repulsion occurs among electrons, either of same species or of two different species. When attraction of force between electron of one species and nucleus of other species predominates, over repulsive force, a bond is formed between the two species. In ionic bond, intensity of force of attraction is found to be maximum. Hence, it is considered as the strong bond or you may say it requires more energy to be broken into its constituent ions. In case of van der Waals' bond intensity of electrostatic force of attraction is much less. Hence, it is a weak bond or you may say it requires less amount of energy to be broken into its constituent ions.

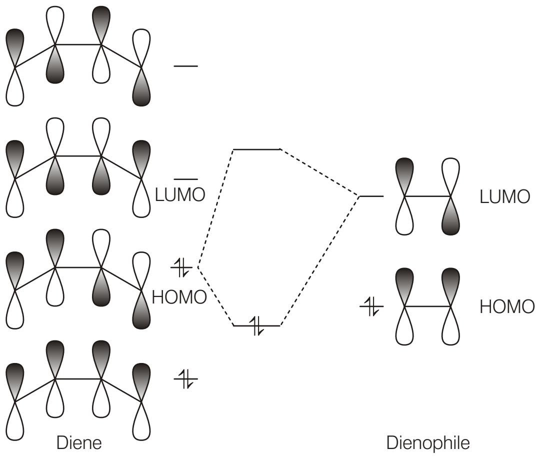
Do you know, why do molecular orbitals of B_2, C_2 and N_2 not follow, the same increasing energy order as O_2 and F_2?

In case of F_2 and O_2, we assume that the interactions between the *s*-orbitals and interactions among the *p*-orbitals are completely independent because of large energy gap between *s* and *p*-orbitals. But in case of B_2, C_2 and N_2 energy gap between *s* and *p*-orbitals is not large. Hence, these orbitals interacts with each other and this interaction is known as ***s-p* mixing**. Generally, orbitals of same symmetry interact together. This means that the $2\sigma_g$-orbitals, derived from the $2s$-orbitals, interact with the $3\sigma_g$-orbitals derived from the $2p_z$-orbitals. Similarly, the *s* and *p*-based σ_u-orbitals interact together, *s-p* mixing leads to stabilisation of $2\sigma_g$ and $2\overset{*}{\sigma}_u$-orbitals and destabilisation of $3\sigma_g$ and $3\overset{*}{\sigma}_u$-orbitals. The destabilisation of the $3\sigma_g$-orbitals is particularly important as they pushes the $3\sigma_g$-orbitals above the $1\pi_u$-orbitals in energy level. The π-orbitals are not affected by *s-p* mixing as these are of wrong symmetry to interact with the *s*-based σ-orbitals.

Do you know, what is the role of HOMOs and LUMOs in Diels Alder reaction?

In Diels Alder reaction conjugated diene and dienophile (alkyne or alkene) react and form cyclohexene and follow concentrated mechanism (bond breaking and bond formation take place simultaneously). In this reaction, HOMO of electron rich species (diene) interacts with LUMO of electron deficient species (alkyne or alkene). This reaction is thermally allowed, provided the orbitals of similar energy.





Note If we use a dienophile with electron releasing group and a diene with an electron withdrawing group then HOMO of dienophile interacts with LUMO of diene.

CHEMISTRY SPECTRUM *for You*

01 Sir, recently I read in a book that lack of vitamin-B_{12} in our body can cause anemia and nervous system damage. I am vegetarian and main source of vitamin-B_{12} is non-vegetarian diet. Is it possible to get essential amount of vitamin-B_{12} from vegetarian diet? Please explain. **[Rohit Sharma, Meerut]**

➥ Dear Rohit, it is a misconception that we could get vitamin-B_{12} only from non-vegetarian diet. It is possible to get vitamin B_{12} from vegetarian diet also. Mostly vitamin B_{12} is available only is animal foods such as meat, fish, eggs and dairy products but you can also get this important nutrient in some nutritional yeasts, as well as from fortified cereals and soy milk.

Keep in mind that you have many choices, when you set a goal of eating fewer animal foods and more plant foods.

You can take various kind of milk fortified with essential amount of vitamin-B_{12} such as almond milk (3 μg), coconut milk (3 μg), soy milk (1.2 μg) and low fat milk (1.15 μg), also you can eat nutritional yeast (2 μg), cereal (0.6 μg), yogurt, (plain low fat, 1.378 μg), cottage cheese (1.07 μg) egg (0.34 μg) and vanilla ice-cream (0.26 μg) .

02 Sir, in case of strong acids or strong bases, I easily solve problems related to pH but for mixture of weak acids I get confused. Please suggest me how can I solve these problems? **[Manoj Jha, Patna]**

➥ Dear Manoj, when mixture of weak acids is given, first you should determine which acid is weaker or act as a base. After this you may go through following steps for solving problems related to finding pH for mixture of weak acids.

Step 1 List the species present before dissociation and identify them as Bronsted-Lowry acids and base.

Step 2 Write balanced equations for all possible proton transfer reactions.

Step 3 Identify the principal reaction the reaction that has the largest equilibrium constant.

Step 4 Make a table that lists the following values for each of the species involved in the principal reaction.

- The initial concentrations
- The change in concentrations on proceeding to equilibrium.
- The equilibrium concentrations.
- During constructing this table define *x* as the concentration (mol/L) of the acid that dissociates.

Step 5 Substitute the equilibrium concentrations into the equation for the principal reaction and solve for *x*.

Step 6 Use the big concentration and equilibrium equations for the subsidiary reactions to calculate the small concentrations of the species involved in the subsidiary equilibrium.

Step 7 Calculate the pH = log $[H_3O^+]$

03 Dear Sir, what is the action of ethyl chloride, which is often used as an anesthetic spray on minor injuries? **[Swati Khurana, New Delhi]**

➥ You put a very good question Swati. Ethyl chloride is a skin refrigerant used in temporary relief of minor sport injuries.

The medium and fine streams are also intended for use as a counterirritant in the management of myofascial pain, restricted motion and muscle tension. The amount of cooling depends of the dosage. Dosage varies with duration of application, the smallest dose needed to produce the desired effect. The anesthetic effect of ethyl chloride rarely lasts more than a few seconds to a minute. This time interval is usually sufficient to help reduce or relieve initial trauma of injury.

Clinical conditions that may respond to Gebauer's ethyl chloride include low back pain, acute stiff neck, acute bursitis of the shoulder, tight hamstrings, sprained ankle, tight master muscles and referred pains due to irritated trigger points. Relief of pain facilitates early mobilisation and restoration of muscle function.

The spray and stretch technique is a therapeutic system that involves three states.

Evaluation, spraying and stretching. The therapeutic value of the spray and stretch technique is most effective when the practitioner has mastered of all the stages and applies them in the proper sequence.

04 Sir, usually I could not solve problems related to determining the formula or oxidation state of the metal in a coordination compound. Please suggest me, how can I solve these kind of problems easily? [Monika Sharma, Pune]

➥ Dear Monika, these kinds of problems can be solved easily, if you keep some basic info about coordination compounds in your mind as I mention below:

For determining the formula of a metal complex

Always remember that charge on the complex is the sum of the charges on metal ion and ligand ions attached to it.

For more clearity you may go through following problems:

***Problem* 1** A cobalt (III) ion forms a complex with four ammonia molecules and two chloride ions. What is the formula of the complex, including its charge?

Sol. The charge on the complex is the sum of the charges on the Co^{3+} ion, the four electrically neutral NH_3 ligands and the two Cl^- ligands,

$$\begin{array}{l} Co^{3+} \quad 4NH_3 \qquad 2Cl^- \\ +3 + (4 \times 0) + [2 \times (-1)] = +1 \end{array}$$

Hence, formula of the complex is $[Co(NH_3)_4Cl_2]^+$.

For determining the oxidation state of the metal in a coordination compound

***Problem* 2** What is the oxidation state of platinum in the coordination compound ?

Sol. As you can clearly see that compound is electrically neutral overall and contains one K^+ cation per complex anion, the anion must have opposite sign, i.e. anion must be $[Pt(NH_3)Cl_5]^-$. Since, ammonia is neutral and chloride has a charge –1, the sum of the oxidation numbers is $1 + n + 0 + 5(-1) = 0$

where, n is the oxidation number of it.

$$K^+ \quad Pt^{n+} \quad NH_3 \quad 5Cl^- = 1 + n + 0 + 5(-1) = 0$$

so, $n = 4$

Case I If complex is positively charged, put the sum of oxidation states of all species within coordination sphere equal to this positive charge.

Case II If complex is negatively charged, put the sum of oxidation states of all species within the coordination sphere equal to this negative charge.

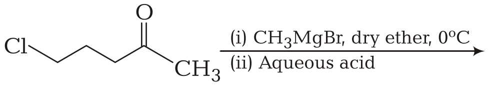
{JEE Advanced Practice}

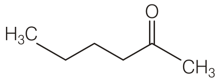
One or More than One Options Correct Type Questions on

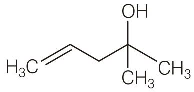
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

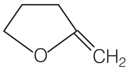
A collection of chapterwise best questions of their types

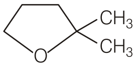
1. The major product in the following reaction is **[2014 Adv.]**



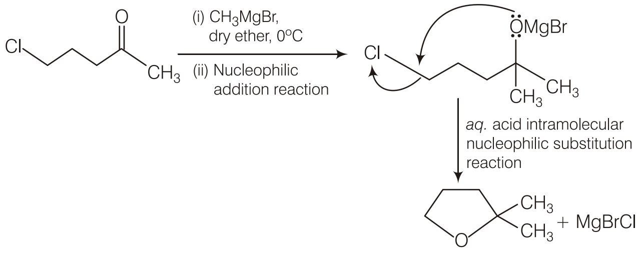
(a)


(b)


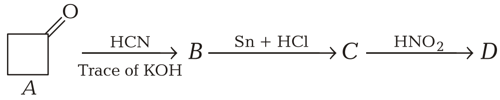
(c)


(d)


Hint



2. Which of the following statements are correct about the reaction given below?



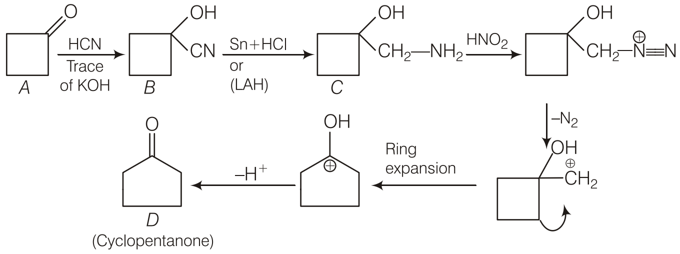
(a) The product *D* is cyclopentanone

(b) The product *D* is α, β-unsaturated cyclopentanone

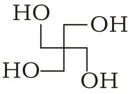
(c) Ring expansion takes place in conversion of *C* to *D*

(d) Conversion of *B* to *C* can also be carried out by using LAH

Hint

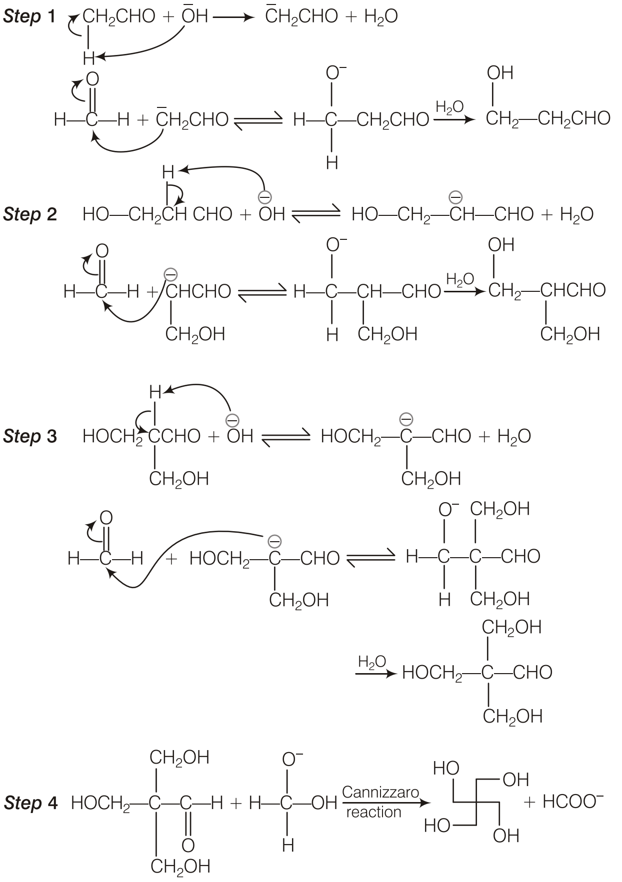


3. The number of aldol reactions that occur in the given transformation is

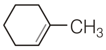
$CH_3CHO + 4HCHO \xrightarrow{conc.aq.NaOH}$


(a) 1 (b) 2 (c) 3 (d) 4

Hint It is an example of repeated aldol condensation followed by Cannizzaro reaction.



4. An organic compound *A* ($C_6H_{10}O$) on reaction with CH_3MgBr followed by acid treatment gives compound *B*. The compound *B* on ozonolysis gives compound *C*, which in presence of a base gives 1-acetylcyclopentene *D*. The compound *B* on reaction with HBr gives compound *E*. Which of the following options are correct about the given information?

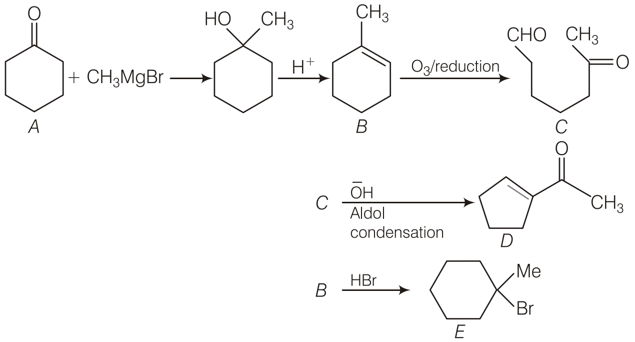
(a) The structure of compound *B* is 

(b) The compound *C* is α, β-unsaturated ketone

(c) The compound *A* contains two double bonds

(d) The structure of compound *E* is 

Hint



5. A new carbon-carbon bond formation is possible in

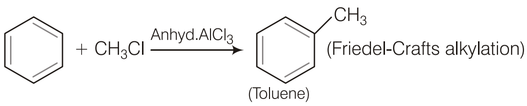
(a) Cannizzaro reaction

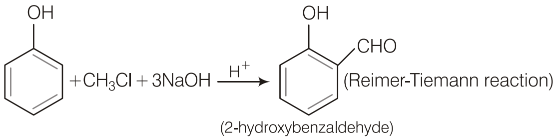
(b) Friedel-Crafts reaction

(c) Clemmensen reduction

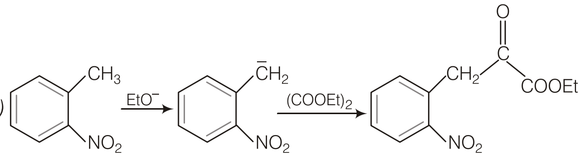
(d) Reimer-Tiemann reaction

Hint

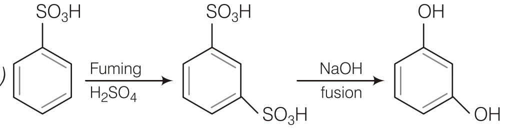


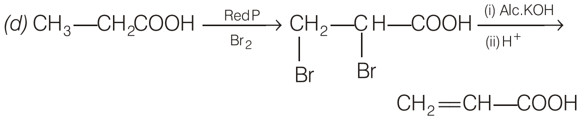


6. Which of the following reaction sequences are correct?

(a) 

(b) $C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{NH_3} C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CH_2NH_2$

(c) 

(d) 

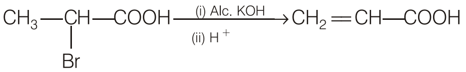
$$CH_3{-}CH_2COOH \xrightarrow[Br_2]{Red\,P} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}COOH \xrightarrow[(ii)\,H^+]{(i)\,Alc.KOH} CH_2{=}CH{-}COOH$$

Hint Correct reaction sequence for option (b) is

$C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{NH_3} C_6H_5CONH_2$

$\xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Ni} C_6H_5CH_2NH_2$

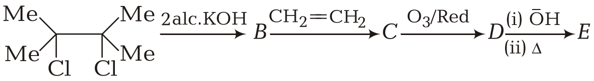
And for option (d) is $CH_3CH_2COOH \xrightarrow[Br_2]{Red\,P}$

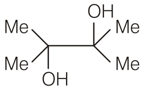


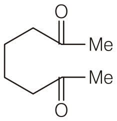
$$CH_3{-}\underset{Br}{CH}{-}COOH \xrightarrow[(ii)\,H^+]{(i)\,Alc.\,KOH} CH_2{=}CH{-}COOH$$

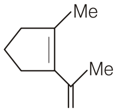
In above reaction step I is Hell-Volhard- Zelinsky reaction.

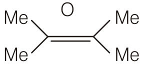
7. For the given reaction, which of the following statements is/are correct?



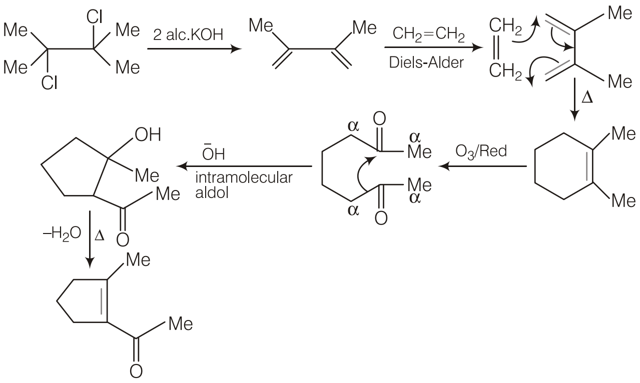
(a) Compound *B* is 

(b) Compound *D* is 

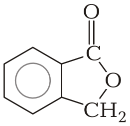
(c) Compound *E* is 

(d) Compound *B* is 

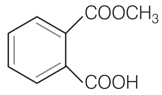
Hint

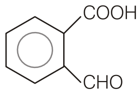


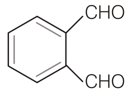
8. Which of the following reactants, on reaction with conc. NaOH followed by acidification gives following lactone as the main product?

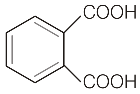


Lactone

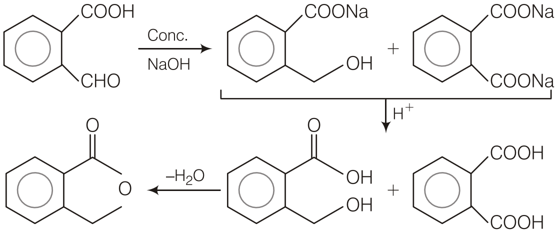
(a)


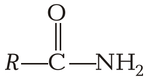
(b)


(c)


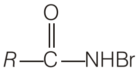
(d)


Hint In option (c) compound undergoes intermolecular Cannizzaro reaction followed by acidification to give lactone.



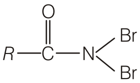


9. Reaction of $R-\overset{O}{\overset{\|}{C}}-NH_2$ with a mixture of Br_2 and KOH gives $R-NH_2$ as the main product. The intermediates involved in this reaction are

(a)

$R-\overset{O}{\overset{\|}{C}}-NHBr$

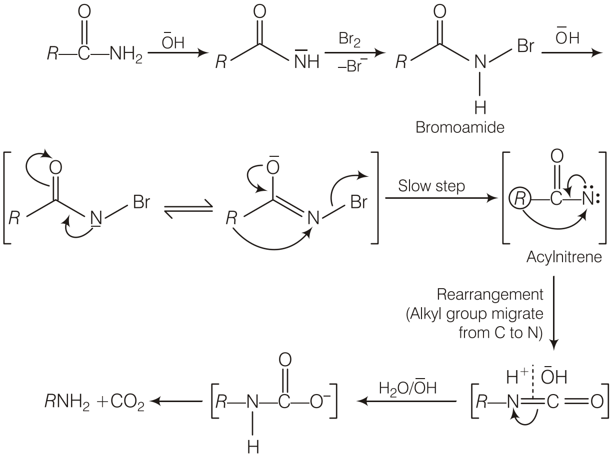
(b) $R-NHBr$

(c) $R-N=C=O$

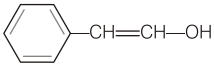
(d)


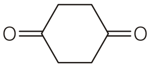
Hint (a,c) This is an example of Hofmann-bromamide rearrangement.

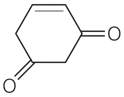
Mechanism

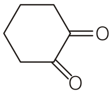


10. Tautomerism is exhibited by

(a)


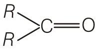
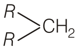
(b)


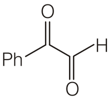
(c)


(d)


Hint All those carbonyl compounds containing α -H to sp^2-carbon show keto-enol tautomerism.

11. Which of the following statements are correct?

(a)

reduced to

this equation represents Clemmensen reduction

(b) The Cannizzaro reaction of

involves intermolecular transfer of hydride

(c) Acetaldehyde and benzophenone give silver mirror test

(d) CH_3CHCl_2 on heating with *aq*.KOH produces acetaldehyde

Hint **Silver Mirror test or Tollen's test**

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Ammonical silver nitrate solution}}{2[Ag(NH_3)_2]^+} + 3\bar{O}H \longrightarrow CH_3COO^- + \underset{\text{Bright silver mirror}}{2Ag} + 2H_2O + 4NH_3$$

$$\underset{\text{Benzophenone}}{Ph_2CO} + 2[Ag(NH_3)_2]^+ + 3\bar{O}H \longrightarrow Ph_2COO^- + 2Ag + 2H_2O + 4NH_3$$

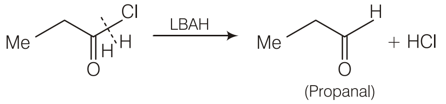
12. Aldehydes and ketones can be reduced to alkanes by

(a) Clemmensen's method
(b) Wolff-Kishner reduction
(c) Meerwein-Ponndorf Verley reaction
(d) Bouveault-Blanc reaction

13. Which of the following reactions would give propanal?

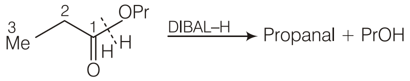
(a) Propanoyl chloride + LBAH
(b) Ethyl cyanide + DBAH
(c) Propyl propanoate + DIBAL-H^+/H_2O
(d) Ethyl propanoate + DBAH (diisobutyl aluminium hydride) $[(i\text{-}C_4H_9)_2AlH]$ at −70° C, followed by hydrolysis

Hint

(a)


(Propanal)

(b) $C_2H_5-C\equiv N \xrightarrow{DBAH/H_2O} C_2H_5-CH=O$ (Propanal)

(c)


(d)


(Propanal)

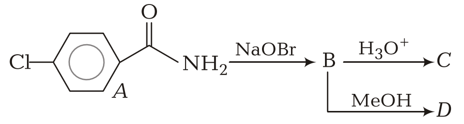
14. Which of the following are examples of aldol condensation?

(a) $2CH_3CHO \xrightarrow{\text{Dil. NaOH}} CH_3CHOHCH_2CHO$
(b) $2CH_3COCH_3 \xrightarrow{\text{Dil. NaOH}} (CH_3)_2C(OH)CH_2COCH_3$
(c) $2HCHO \xrightarrow{\text{Dil. NaOH}} CH_3OH$
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{Dil. NaOH}} C_6H_5CH_2OH$

Hint For aldol condensation, reactant should have α-hydrogen atoms, so that they can undergo aldol condensation. Option (c) is an example of Cannizzaro reaction.

Option (d) is an example of Claisen-Schmidt reaction.

15. Which of the following statements are correct for the given equation?

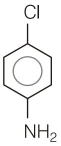


(*a*) It is an example of Lossen rearrangement reaction

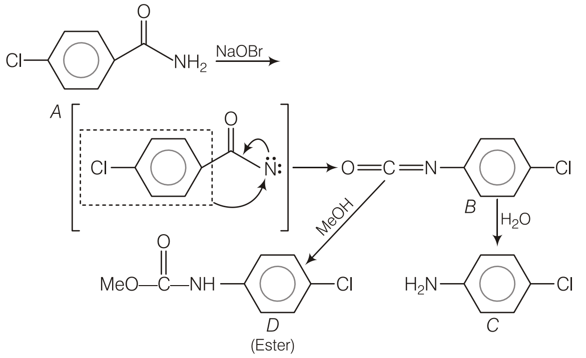
(*b*) It is an example of Hofmann bromamide rearrangement reaction

(*c*) The product formed *D* is an ester

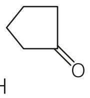
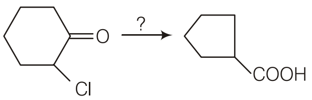
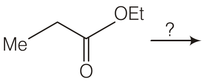
(*d*) The compound formed *C* is



Hint The given equation is an example of Hofmann bromamide rearrangement reaction.

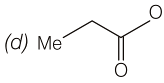


16. Which of the following options are correctly matched?

	Reaction		Characteristics/ reagent
(a)	Diethyl adipate $\xrightarrow{?}$ 	⇒	(i) NaH/EtOH (ii) H_3O^+ (iii) Δ
(b)	$RCOCl \xrightarrow{?} RCOOH$	⇒	(i) EtONa/EtOH (ii) H_3O^+ (iii) Δ
(c)		⇒	(i) Zn (ii) $Me_2C{=}O$ (iii) H_2O
(d)	 $\xrightarrow{?}$ Pentan-3-one	⇒	(i) $\overset{\ominus}{O}H$ (ii) H_2O, H_3O^+

Hint

(*b*) $RCOCl \xrightarrow[\text{(ii) } Ag_2O/Pt \quad \text{(ii) } H_2O]{\text{(i) } CH_2N_2} RCH_2COOH$ (Arndt-Eistert rearangement)

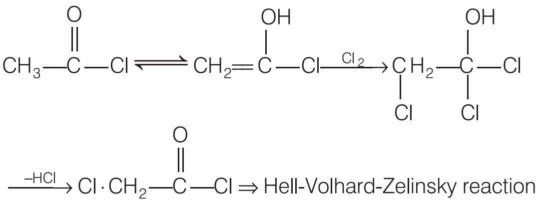
(*d*)  $\xrightarrow[\text{(ii) } H_3O^+ \quad \text{(iii) } H_2O]{\text{(i) EtONa/EtOH}}$ Pentan-3-one

(It is an example of Claisen ester condensation).

17. Which of the following name reactions are correctly matched?

(*a*) $RCOCl \xrightarrow[Pd\text{-}BaSO_4]{H_2} RCHO \xrightarrow{H_2} RCH_2OH$ ⇒ Rosenmund's reduction

(*b*)

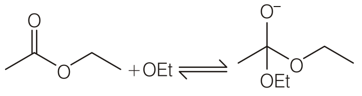


$CH_3-\overset{O}{\overset{\|}{C}}-Cl \rightleftharpoons CH_2{=}\overset{OH}{\overset{|}{C}}-Cl \xrightarrow{Cl_2} \underset{Cl}{\underset{|}{C}}H_2-\overset{OH}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-Cl$

$\xrightarrow{-HCl} Cl\cdot CH_2-\overset{O}{\overset{\|}{C}}-Cl$ ⇒ Hell-Volhard-Zelinsky reaction

(*c*) $RCONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

⇒Hofmann-bromamide reaction.

(*d*) 

⇒ Aldol condensation reaction

Hint Option (d) is an example of Claisen condensation reaction.

18. Which of the following statements is/are incorrect?

(*a*) Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide

(*b*) γ-keto pentanal forms a dioxime and gives negative iodoform test and Tollen's test

(*c*) 2-pentanone does not reduce Fehling's solution, forms a phenyl hydrazone and shows a haloform reaction.

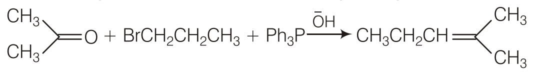
(*d*) Acid chlorides easily give ketone with *R*Mg*X* but fail with R_2Cd

Hint γ-keto pentanal forms a dioxime and gives positive iodoform and Tollen's test.

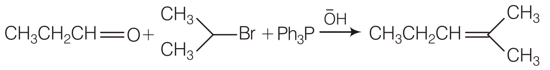
Acid chlorides fail to give ketone with *R*Mg*X*, but with R_2Cd ketone is obtained easily. It is because $\overset{\delta-}{C}-\overset{\delta+}{Cd}$ bond is more covalent than $\overset{\delta-}{C}-\overset{\delta+}{Mg}$ bond. Since, Cd is less electropositive than Mg. Therefore, *R* of R_2Cd is not nucleophilic enough to add to $>C{=}O$.

The Grignard reagent reacts faster with any ketone to produce a 3°-alcohol.

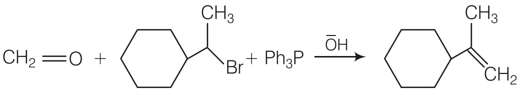
19. Which of the methods are better in the synthesis of the following compounds by wittig reagent?

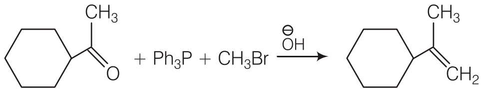
(*a*) 

$(CH_3)_2C{=}O + BrCH_2CH_2CH_3 + Ph_3P \xrightarrow{\bar{O}H} CH_3CH_2CH{=}C(CH_3)_2$

(*b*) 

$CH_3CH_2CH{=}O + (CH_3)_2CH\text{-}Br + Ph_3P \xrightarrow{\bar{O}H} CH_3CH_2CH{=}C(CH_3)_2$

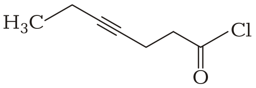
(*c*) 

(*d*) 

Hint The methods (a) and (d) are better in the sythesis of products by wittig reaction because it proceeds by S_N2 mechanism. The reactivity of *RX* in S_N2 reaction is 1° > 2° > 3° *RX* and in (a) and (d) 1° *RX* is used.

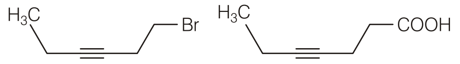
20. In the following sequence, products A, B and C are formed represents a reagent.

$$\text{Hex-3-ynal} \xrightarrow[\text{(ii) PBr}_3]{\text{(i) NaBH}_4} A \xrightarrow[\text{(ii) CO}_2\ \text{(iii) H}_3\text{O}^+]{\text{(i) Mg/ether}} B \xrightarrow{C}$$

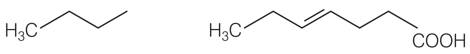


The structure of compounds A, B and C, respectively are

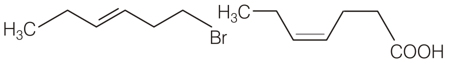
A *B* *C*

(a)


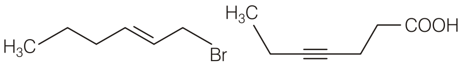
$SOCl_2$

(b)


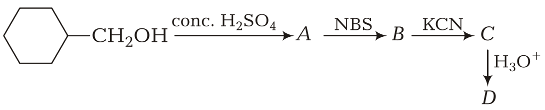
PCl_2

(c)


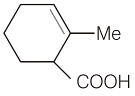
PCl_3

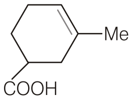
(d)


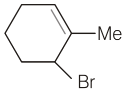
S_2OCl_2

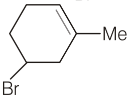
21.


Which of the following are correct for the given reaction?

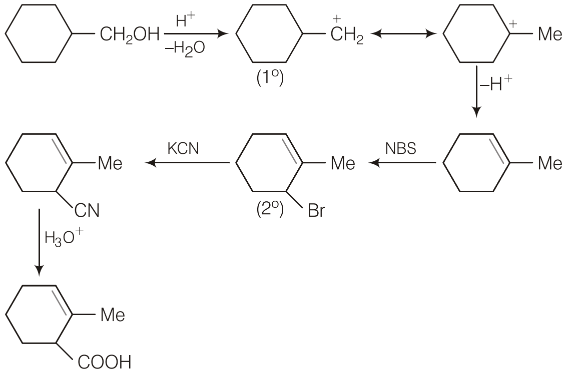
(a) The compound formed *D* is


(b) The compound formed *D* is


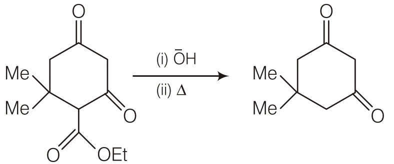
(c) The compound formed *B* is


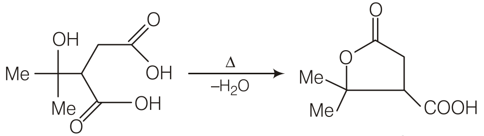
(d) The compound formed *B* is


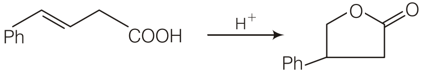
Hint

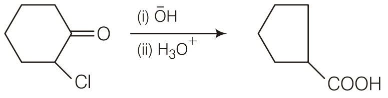


22. Which of the following reactions are correct?

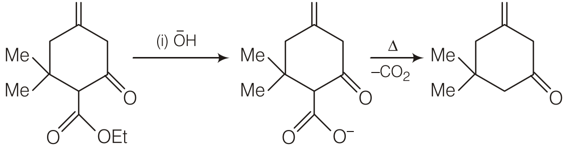
(a)


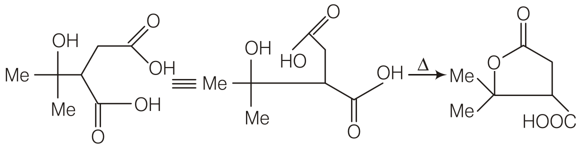
(b)


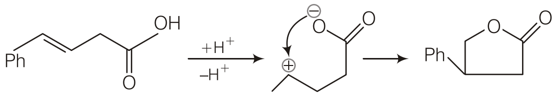
(c)


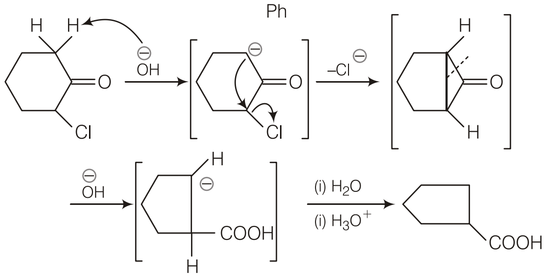
(d)


Hint

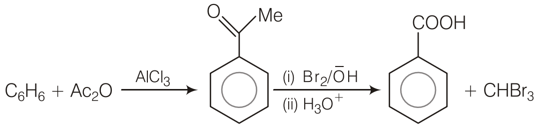
(a)


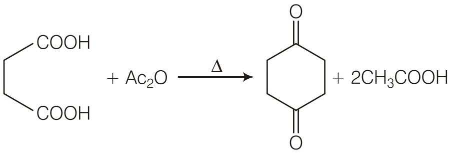
(b)


(c)


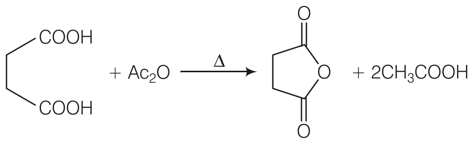
(d)


23. Which of the following reactions are correct?

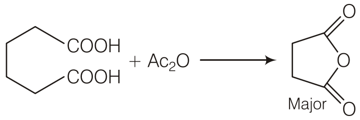
(a)


(b)


(c)

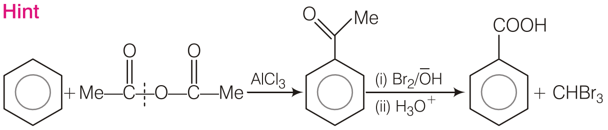


(d)

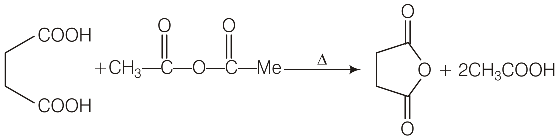


Hint

(a)

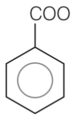


(c)

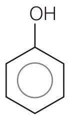


24. The compound(s) soluble in *aq*. NaOH solution is/are

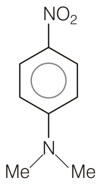
(a)



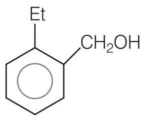
(b)



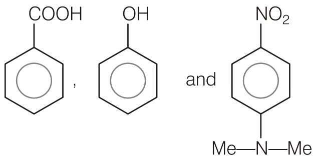
(c)



(d)

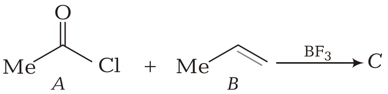


Hint



are acidic in nature and hence soluble in *aq*.NaOH.

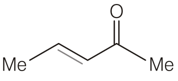
25. Which of the following statements are correct about the given reaction?



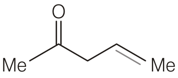
(a) The formation of (*C*) proceeds through the formation of carbocation.

(b) The formation of (*C*) proceeds through the formation of acyllium ion.

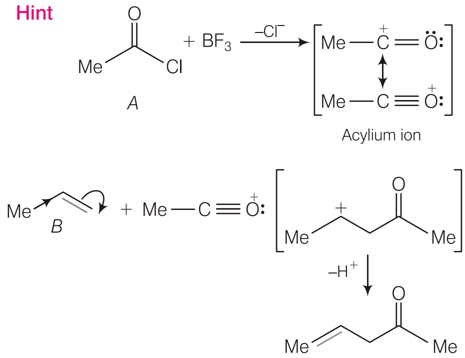
(c) The product (*C*) is



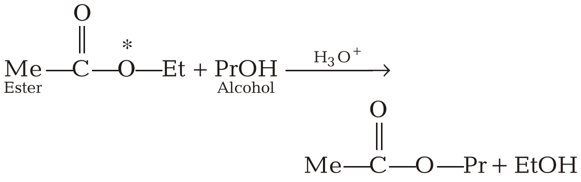
(d) The product (*C*) is



Hint



26. Which of the following statements are correct about the *trans*-esterification reaction, catalysed by H_3O^+ (H_2SO_4 or dry HCl) or RO^- (EtONa)?



$$\underset{\text{Ester}}{Me}-\overset{O}{\overset{\|}{C}}-\overset{*}{O}-Et + \underset{\text{Alcohol}}{PrOH} \xrightarrow{H_3O^+} Me-\overset{O}{\overset{\|}{C}}-O-Pr + EtOH$$

(a) Rate of *trans*-esterification is dependent on the concentration of ester

(b) Isotopic oxygen is present in the new alcohol ($Et\overset{*}{O}H$) formed

(c) It involves tetrahedral intermediate in which the hybridisation of C of the ($C=O$) group changes sp^2 to sp^3

(d) Alcohol (PrOH) is taken in excess to shift the equilibrium to RHS

Hint The rate of *trans*-esterification does not depend only on the concentration of ester.

27. Among the following compounds, which will react with acetone to give a product containing $>C=N-$?

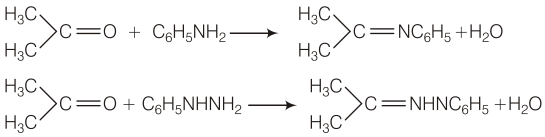
(a) $C_6H_5NH_2$

(b) $(CH_3)_3N$

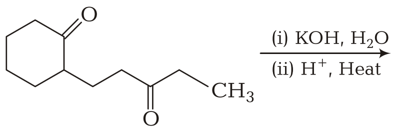
(c) $C_6H_5NHC_6H_5$

(d) $C_6H_5NHNH_2$

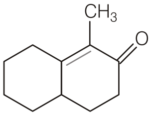
Hint



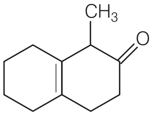
28. The major product of the following reaction is



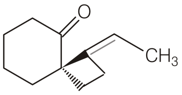
(a)



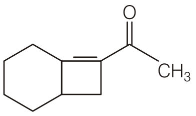
(b)



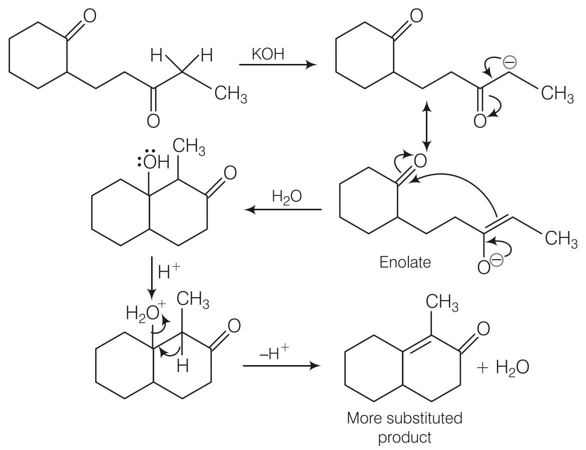
(c)



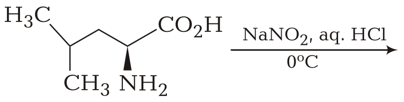
(d)



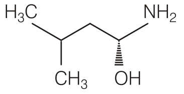
Hint



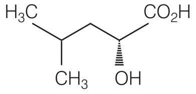
29. The major product of the reaction is **(2015 Adv.)**



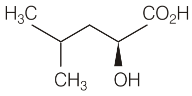
(a)



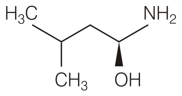
(b)



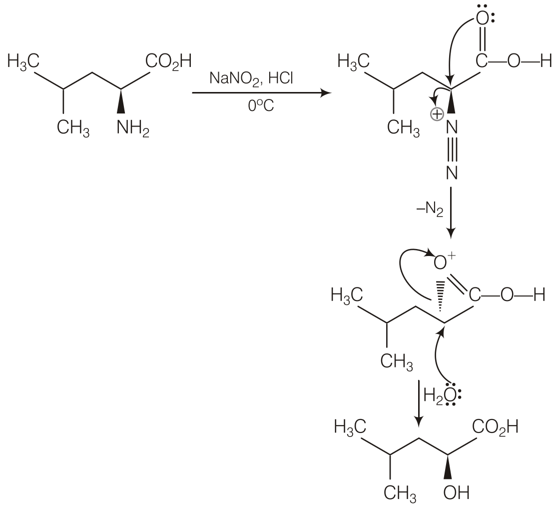
(c)



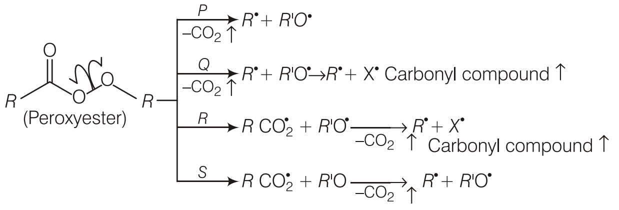
(d)



Hint

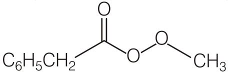


30. Different possible thermal decomposition pathways for peroxyesters are shown below.

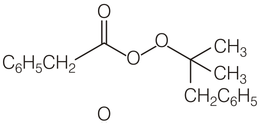


Which of the following options are correctly match?

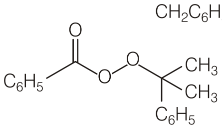
(a) Pathway $P \longrightarrow$



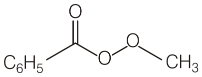
(b) Pathway $Q \longrightarrow$



(c) Pathway $R \longrightarrow$

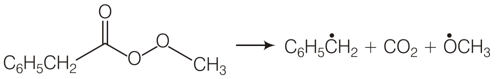


(d) Pathway $S \longrightarrow$

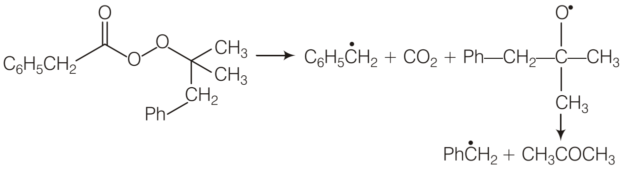


Hint For solving this problem we can check stability of radical obtained after fragmentation of peroxyester.

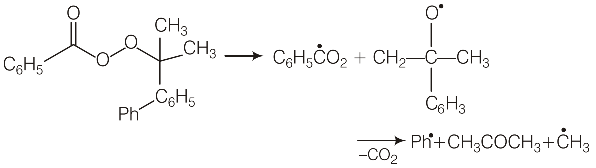
For option (a)



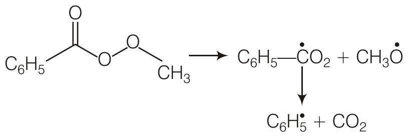
For option (b)



For option (c)



For option (d)



Answers

1. (d)	**2.** (a,c,d)	**3.** (c)	**4.** (a,b,d)	**5.** (b,d)	**6.** (a,c)	**7.** (b,c)	**8.** (b,c)	**9.** (a,c)	**10.** (a,d)
11. (a,c,d)	**12.** (a,b)	**13.** (a,b,c,d)	**14.** (a,b)	**15.** (b,c,d)	**16.** (a,b)	**17.** (a,b,c)	**18.** (b,d)	**19.** (a,d)	**20.** (a)
21. (a,c)	**22.** (a,b,c,d)	**23.** (a,c)	**24.** (a,b,c)	**25.** (b,c)	**26.** (b,c,d)	**27.** (a,d)	**28.** (a)	**29.** (c)	**30.** (a,b,c,d)

TARGET CBSE 2016

TEST Zoom

Simulator Test Series to Zoom up Your Board Preparations

Board Exam Scale UP

Questions to Measure Your Problem Solving Skills

General Instructions

1. *All questions are compulsory.*
2. *Q. no. 1 to 5 are very short answer questions and carry 1 mark each.*
3. *Q. no. 6 to 10 are short answer questions and carry 2 marks each.*
4. *Q. no. 11 to 22 are also short answer questions and carry 3 marks each.*
5. *Q. no. 23 is a value based question and carry 4 marks.*
6. *Q. no 24 to 26 are long answer questions and carry 5 marks each.*

❶ Very Short Answer Type Questions

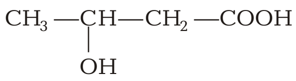
1. Which one out of NH_3 and CO_2, will be adsorbed more readily on the surface of charcoal? Give reason.

Hint NH_3, as it has greater intermolecular forces of attraction.

2. Out of benzyl chloride and cyclohexyl chloride, which one would undergo S_N2 reaction faster and why?

Hint Cyclohexyl chloride would react faster because benzyl chloride is more stable due to +*I*-effect and resonance.

3. Write the IUPAC name of the compound.



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-COOH$$

Hint 3-hydroxybutanoic acid

4. Complete the following chemical equation,

$$P_4 + 10SO_2Cl_2 \longrightarrow$$

Hint $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2\uparrow$

5. Which point defect in crystals of a solid does not change the density of the solid?

Hint Frenkel defect

❷ Short Answer Type Questions

6. Draw the structure of the following compounds:

(i) $H_2S_2O_8$

(ii) $H_2S_2O_7$

7. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant, if the conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3}\ Sm^{-1}$?

Hint Cell constant = Conductivity (κ) × Resistance (*R*)

8. Write the IUPAC name of

(i) $[Pt(NH_3)_3NOCl_2]Br_2$

(ii) $[Cr(NH_3)_2Cl_4]Cl$

Hint (i) Triamminedichloridonitrosylplatinum (IV) bromide.

(ii) Tetraamminedichloridochromium (III) chloride.

9. Describe the following giving the relevant chemical equation in each case:

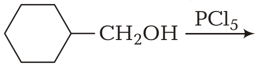
(i) Carbylamine reaction

(ii) Hofmann's bromamide reaction

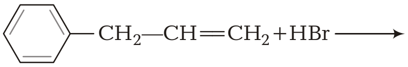
or

Draw the structures of major monohalo products in each of the following reactions:

(i)

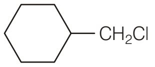


(ii)

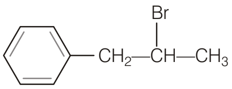


Hint

(i)

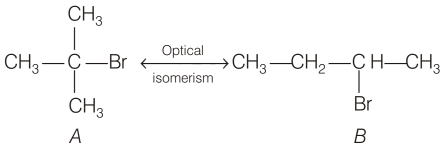


(ii)



10. Compound *A* having molecular formula C_4H_9Br reacts with *aq.*KOH solution. The rate of reaction depends upon the concentration of the compound *A* only. When another optically active isomer *B* of this compound reacts with *aq.* KOH solution then rate of reaction is found to be dependent on concentrations of compound *A* and KOH both. Write down the structural formulae for both compounds *A* and *B*.

Hint



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \xleftrightarrow[\text{isomerism}]{\text{Optical}} CH_3-CH_2-\underset{Br}{\underset{|}{C}}H-CH_3$$

A *B*

❸ Short Answer Type Questions

11. Give reasons for the following:

(i) $(CH_3)_3P{=}O$ exists but $(CH_3)_3N{=}O$ does not.

(ii) Oxygen has less electron gain enthalpy with negative sign than sulphur.

(iii) H_3PO_2 is a stronger reducing agent than H_3PO_3.

Hint (i) Nitrogen cannot form $d\pi$-$p\pi$ multiple bond, while phosphorus can form $d\pi$-$p\pi$ multiple bond.

(ii) Because size of oxygen is smaller than sulphur.

(iii) The acids which contain P—H bonds, have strong reducing properties.

12. At 25°C, the vapour pressures of benzene (C_6H_6) and toluene (C_7H_8) are 93.4 torr and 26.9 torr, respectively. A solution is made by mixing 35.0 g of benzene and 65.0 g of toluene. At what applied pressure, in torr, will this solution boil at 25°C?

Hint $p_{C_6H_5CH_3} = p^{\circ}_{C_6H_5CH_3} \cdot \chi_{C_6H_5CH_3}$

$$p_{total} = p_{C_6H_6} + p_{C_6H_5CH_3} = 52.7 \text{ torr.}$$

13. Find the stability constant of the complex $[Zn(NH_3)_4]^{2+}$ formed in the reaction,

$$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$$

Given that, $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ V

and $E^{\circ}_{[Zn(NH_3)_4]^{2+}/Zn,\ 4NH_3} = 1.03$V

Hint $E^{\circ}_{cell} = \dfrac{0.0591}{n}\log k;\ k = 1.371 \times 10^9$

14. Explain, why

(i) Noble gases have very low melting and boiling points?

(ii) Neon is used in illuminating warning signal?

(iii) ICl is more reactive than I_2?

15. (i) Write the electronic configuration of $[Fe(CN)_6]^{4-}$ on the basis of crystal field splitting theory.

(ii) Why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM, whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM?

(iii) What type of isomerism is shown by $[Co(NH_3)_3NO_2]^{2+}$ and $[Co(NH_3)_3ONO]^{2+}$?

Hint (i) $t_{2g}^{6}\ e_g^{0}$

(ii) CN^- ligand produces strong field means splitting of *d*-orbitals will be large, whereas H_2O ligand produce weak field means splitting of *d*-orbital will be small.

(iii) Linkage isomerism

16. (i) Describe Bredig's Arc method briefly.

(ii) Define collodion.

(iii) Some reactants give different products using different catalysts. Explain why?

17. Account for the following.

(i) Primary amines $(R{-}NH_2)$ have higher boiling points than tertiary amines (R_3N).

(ii) Aniline does not undergo Friedel-Crafts reaction.

(iii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

Hint (i) Intermolecular hydrogen bonding is present in primary amines.

(ii) Aniline with $AlCl_3$(catalyst) forms salt.

(iii) Basic strength depends upon the stabilisation of the conjugate acids by H-bonding, steric hindrance and $+I$-effect.

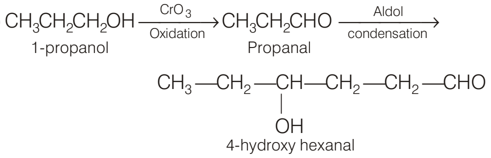
18. Bring out the following conversions:

(i) 1-propanol to 4-hydroxyhexanal.

(ii) Bromobenzene to 1-phenylethanol.

(iii) Benzene to *m*-nitroacetophenone.

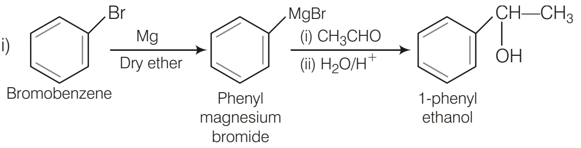
Hint (i)



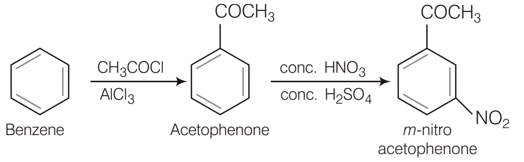
$$\underset{\text{1-propanol}}{CH_3CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{CrO_3} \underset{\text{Propanal}}{CH_3CH_2CHO} \xrightarrow[\text{condensation}]{\text{Aldol}}$$

$$\underset{\text{4-hydroxy hexanal}}{CH_3-CH_2-\underset{OH}{\underset{|}{C}H}-CH_2-CH_2-CHO}$$

(ii)

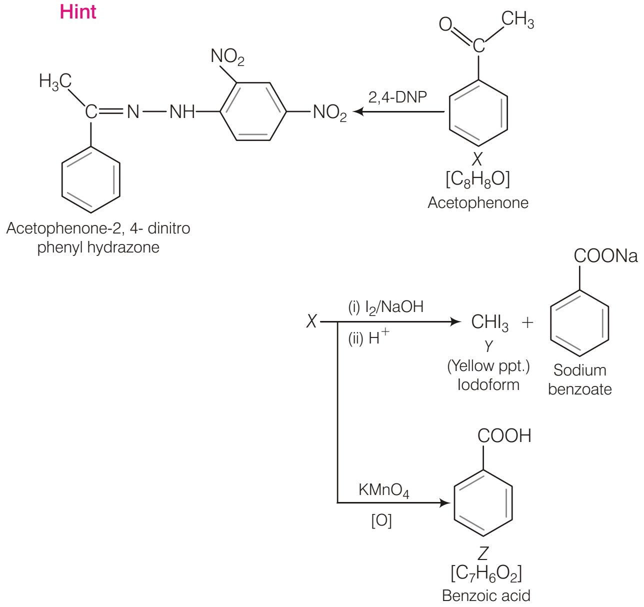


(iii)



19. An aromatic compound *X* (molecular formula, C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound *Y* on treatment with iodine and sodium hydroxide solution. Compound *X* does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate it forms a carboxylic acid *Z* (molecular formula, $C_7H_6O_2$), which is also formed alongwith the yellow compound in the above reaction. Identify *X*, *Y* and *Z* and write all the reactions involved.

Hint



20. (i) Give two examples of macromolecules that are chosen as drug targets.

(ii) What are antiseptics? Give an example.

(iii) Why is use of aspartame limited to cold foods and soft drinks?

or

Write the name of atleast one polymer used for making of following materials, alongwith writing the monomer(s) of them.

(i) Synthetic fibres (ii) Electrical switches

(iii) Paints and lacquers

Hint (i) Nucleic acids, proteins.

(ii) For example - H_2O_2

(iii) Aspartame decomposes at baking or cooking temperatures.

or

(i) Nylon-6,6 [Monomers: Adipic acid and hexamethylenediammine].

(ii) Bakelite [Monomers: Phenol and formaldehyde].

(iii) Glyptal [Monomers: Ethylene glycol and phthalic acid].

21. Write the chemical equations for the following reactions:

(i) Stephen reaction

(ii) Etard reaction

(iii) Hell-Volhard-Zelinsky (HVZ) reaction.

22. (i) Write the structural difference between a nucleoside and a nucleotide.

(ii) Justify that the two strands of DNA are complimentary and not the identical one.

Hint (i) When nucleoside is linked to phosphoric acid at 5-position of sugar moiety, we get a nucleotide.

(ii) The two strands of DNA are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.

④ Value Based Question

23. Mohan, a class 12th student fainted, while playing badminton in his school. Mr. Naveen, the sports teacher in his school immediately fetched him a glass of glucose water and took him to a nearby hospital, where he was diagnosed with 'acute anaemia.'The doctor prescribed him, iron and multivitamis supplements. Mr. Naveen paid the medical bills. After sometime Mohan was diagnosed to be normal.

Answer the following questions based on the given passage:

(i) Name the vitamin whose deficiency causes anaemia.

(ii) Name the protein which is composed of iron and is found in blood.

(iii) Why Mr. Naveen immediately fetched glucose water to Mohan?

(iv) What are the values associated with Mr. Naveen?

Hint (i) Vitamin-B_{12}

(ii) Haemoglobin

(iii) Glucose provides instant energy, as it does not need to be digested.

(iv) Mr. Naveen is knowledgeable, caring and responsible.

⑤ Long Answer Type Questions

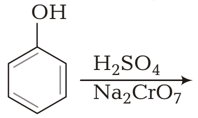
24. (i) How many alcohols with molecular formula, $C_4H_{10}O$ are chiral in nature?

(ii) How are the following conversions carried out

(a) phenol to acetophenone

(b) ethanol to methanol?

(iii) Write the IUPAC name of the major product obtained in the following reaction.

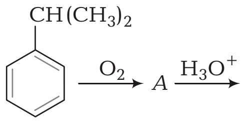


or

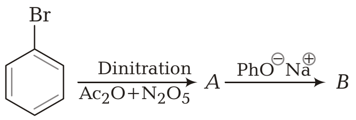
(i) Write the mechanism of the reaction of acid (H_2SO_4) with ethene.

(ii) Identify A and B in the following reactions:

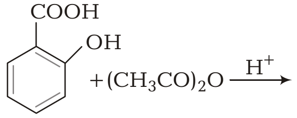
(a)



(b)



(iii) Give the structure and the IUPAC name of the major product obtained in the following reaction:



25. (i) Complete the following chemical equations.

(a) $Cr_2O_7^{2-}\ (aq) + H_2S\ (g) + H^+\ (aq) \longrightarrow$

(b) $Cu^{2+}\ (aq) + I^-\ (aq) \longrightarrow$

(ii) How would you account for the following?

(a) The oxidising power of oxo anions are in the order: $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

(b) The third ionisation enthalpy of manganese $(Z = 25)$ is exceptionally high.

(c) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

or

(i) Metallic radii of few transition elements are given below.

Elements	Fe	Co	Ni	Cu
Metalic radii\ pm	126	125	125	128

Arrange these elements in increasing order of their densities.

(ii) Write the reaction involve, when $K_2Cr_2O_7$ solution is added to Sn^{2+} ion.

(iii) Colour of $KMnO_4$ disappears, when oxalic acid is added to its solution in acidic mediun.

Hint

(i) (a) $Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O\ (l)$

(b) $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(g)$

(ii) (a) It is because V in its lower oxidation state is less stable than Cr which in turn is less stable than Mn.

(b) Because the third electron has to be removed from stable half-filled 3*d*-orbitals.

(c) $d^4 \rightarrow d^3$ transition occurs in Cr^{2+} to Cr^{3+}, while $d^6 \rightarrow d^3$ transition occurs in Fe^{2+} to Fe^{3+}.

or

(i) Increasing order of densities of the metals are:

$$Fe < Co < Ni < Cu$$

(ii)

Oxidation

$$Cr_2O_7^{2-} + 14\overset{+}{H} + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

Reduction

(iii) Due to addition of oxalic acid, Mn^{7+} (coloured) reduce to Mn^{2+} (colourless).

26. (i) Plot the graph between concentration and time for a zero order reaction.

(ii) The following results have been obtained during the experiments based on kinetic studies of the reaction.

$$2A + B \longrightarrow C + D$$

Exp.no	$[A]$/mol L^{-1}	$[B]$/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
1.	0.1	0.1	6.0×10^{-3}
2.	0.2	0.2	7.2×10^{-2}
3.	0.3	0.4	2.88×10^{-1}
4.	0.4	0.1	2.40×10^{-2}

Calculate the rate law and the rate constant for the above reaction.

or

(i) For a first order reaction, show that time required for 99% completion is twice, the time required for the completion of 90% of reaction.

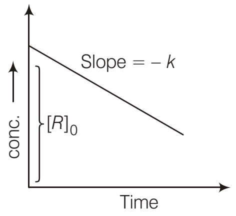
(ii) Consider the following first order gas phase decomposition reaction

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

The initial pressure of the system was p. After lapse of time t total pressure of the system was increased by a units and became p_x. Find the rate constant (k) for the reaction.

Hints

(i)



(ii) Rate $= k[A][B]^2$

Rate constant $= 6.0\ mol^{-2}\ L^2\ min^{-1}$

or

(i) $t = \dfrac{2.303}{k} \log \dfrac{\text{Initial concentration}}{\text{Final concentration}}$

$$t_{99\%} = \frac{2.303}{k} \log \frac{100}{1} = \frac{4.606}{k}$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{10} = \frac{2.303}{k}$$

$$\Rightarrow \quad t_{99\%} : t_{90\%} = 2:1$$

(ii) Rate constant, $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i - p_t}$

Notice Board

IPU CET will be on May 8, 2016

Indraprastha University Common Entrance Test (IPU CET) 2016 will be conducted on May 8 (Sunday), 2016 for admissions to various UG engineering programmes, says a notification by the conducting authority. According to the notification released by Guru Gobind Singh Indraprastha University, IPU CET 2016 will be held between 2 pm to 4.30 pm on May 8, 2016 for admissions to B. Tech programmes, while the result will be declared latest by May 24, 2016. Candidates, who fulfill the eligibility criteria and wish to appear in IPU CET 2016, need to fill up the application form and submit it till March 29, 2016 (upto 4 pm).

TARGET CBSE 2016

TEST Zoom

Simulator Test Series to Zoom up Your Board Preparations

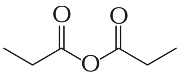
Board Exam Scale UP

Questions to Measure Your Problem Solving Skills

1. What is the covalency of nitrogen in N_2O_5?

Hint Covalency is the number of shared pair of electrons by an atom in a compound.

2. Write the IUPAC name of the given compound,



Hint Propanoyl propanoate

3. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason.

Hint According to Hardy-Schulze rule, greater the valency of the flocculating ion added to the colloid, greater is its power to cause coagulation.

4. Which of the following is a natural polymer?
Buna-S, Proteins, PVC.

Hint Proteins.

5. A compound contains two types of atoms *X* and *Y*. It crystallises in a cubic lattice with atoms *X* at the corners of the unit cell and atom *Y* at the body-centred. What is the formula of the compound?

Hint The formula of the compound is *XY*.

6. What is lanthanoid contraction? What is its effect on the chemistry of the elements, which follow the lanthanoids?

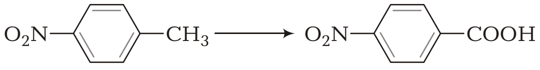
Hint The radii of the members of 3rd transition series is very similar to those of 2nd transition series and hence, have same physical and chemical properties.

7. State Kohlrausch's law of independent migration of ions. Why does the conductivity of a solution decrease with dilution?

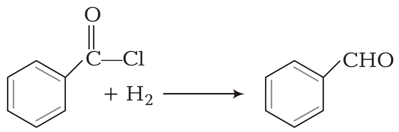
Hint The conductivity of a solution is related with the number of ions present per unit volume of the solution.

8. Name the reagents used in the following reactions:

(i)



(ii)



Hint (i) $KMnO_4$-KOH (ii) Rosenmund reduction

9. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water, has an osmotic pressure of 0.335 torr at 25°C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass.

or

How much urea (molar mass = 60 g $\text{mol}^{\ 1}$) should be dissolved in 50 g of water, so that its vapour pressure at room temperature is reduced by 25%. Calculate the molality of the solution obtained.

Hint $M_2 = \frac{wRT}{V} = 14193.3\ \text{g mol}^{\ 1}$

or

$$\frac{p° \quad p_s}{p°} = \frac{w_2 / m_2}{w_1 / m_1 + w_2 / m_2} = x_2 \text{ and Molality} = \frac{w_2 \quad 1000}{m_2 \quad w_1}$$

10. (i) Write the Nernst equation and compute the emf of the following cell at 298 K.

$Sn(s)\,|Sn^{2+}(0.05M) \quad H^+ \ (0.02M)\,H_2,\ 1\,\text{atm} \ \ Pt$

Given that $E°_{Sn^{2\ +}/Sn} = \quad 0.14\ V$

(ii) Calculate the degree of dissociation of acetic acid at 298 K. Given that

$_{m(CH_3COOH)} = 11.70\ S\ cm^2\,mol^{\ 1}$

$^{\circ}_{m(CH_3COO\ \ )} = 40.90\ S\ cm^2\,mol^{\ 1}$

$^{\circ}_{m(H^+)} = 349.1\ S\ cm^2\,mol^{\ 1}$

Hint (i) $E_{cell} = E°_{cell} \quad \frac{0.059}{n} \log \frac{[Sn^{2+}]}{[H^+]^2} \sim 0.08V;\ E_{cell} = 0.14\ V$

(ii) Degree of dissociation, $= \frac{_m}{^{\circ}_m} = 3.0 \quad 10^{\ 2}$

{BOARD EXAM SCALE UP}

11. (i) In reference to Freundlich adsorption isotherm, write the expression for adsorption of gases on solids in the form of an equation.

(ii) Write an important characteristic of lyophilic sols.

(iii) Based on the type of particles of dispersed phase, give one example of each associated colloid and multimolecular colloid.

Hint (i) $\frac{x}{m} = Kp^{1/n}$

(ii) Lyophilic sols are reversible sols. These are quite stable and cannot be coagulated.

(iii) Associated colloid e.g. Soap
Multimolecular colloid e.g. Gold sol.

12. (i) How do we separate two sulphide ores by froth floatation method? Explain with an example.

(ii) Give two requirements for vapour phase refining.

(iii) How is copper extracted from low grade copper ores?

Hint

(i) In this method, the surface of sulphide ores is preferentially wetted by oil, while that of gangue is preferentially wetted by water.

(ii) (a) The metal should form a volatile compound with a suitable reagent.

(b) The volatile compound should be easily decomposable so that we can get pure metal easily.

(iii) Leaching.

13. Silver crystallises in fcc lattice, if the edge length of the unit cell is $4.07 \quad 10^{8}$ cm and the density of the crystal is 10.5 g cm ^{3}, calculate the atomic mass of silver. [$N_A = 6.02 \quad 10^{23}$ atoms mol ^{1}]

Hint Density, $d = \frac{Z \quad M}{a^3 \quad N_A}$ $M = 106.54$ g mol ^{1}

14. (i) How would you account for the followings?

(a) $E°$ values for Mn, Ni and Zn are more negative than expected.

(b) The halides of transition elements becomes more covalent with increasing oxidation state of the metal.

(ii) Complete the reaction, $Cr_2O_7^{2} \ + 8H^+ + 3H_2S$ ¾

Hint (i) (a) Mn^{2+} and Zn^{2+} have half-filled and completely filled configurations respectively. For, Ni^{2+}, $E°$ value is related to the highest negative enthalpy of hydration.

(b) As per Fajan's rule, as the size of metal ion decreases, covalent character of the bond formed increases

(ii) $Cr_2O_7^{2} \ + 8H^+ + 3H_2S$ ¾ $2Cr^{3+} + 7H_2O + 3S$

15. (i) Write all the geometrical isomers of complex $[Pt(NH_3)(Cl)(Py)(Br)]$ and how many of these will exhibit optical isomerism?

(ii) What happens to the colour of coordination compound $[Ti(H_2O)_6]Cl_3$ when heated gradually?

(iii) Why coordination complexes are preferred in the electrolytic bath for electroplating?

Hint (i) Three geometrical isomers are possible and none will exhibit optical isomerism.

(ii) Its colour becomes lighter on heating.

(iii) Electroplating of metals involves the use of complex salts as electrolytes. $K[Ag(CN)_2]$ is extensively used in silver plating.

16. The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte X is 100 at 40°C. The same conductivity cell filled with 0.01 M solution of electrolyte Y, has a resistance of 50 . The conductivity of 0.05M solution of electrolyte X is $1.0 \quad 10^{4}$ S cm ^{1}. Calculate

(i) cell constant

(ii) conductivity of 0.01M Y solution

(iii) molar conductivity of 0.01M Y solution.

Hint (i) Cell constant, $G \ = \text{Resistance } (R) \quad \text{Conductivity } (\ )$

$= 10^{\ 2}\text{cm}^{\ 1}$

(ii) Conductivity, $\ = \frac{\text{Cell constant}(G^*)}{\text{Resistance}(R)} = 2 \quad 10^{\ 4}\text{S cm}^{\ 1}$

(iii) Molar conductivity, $_m = \frac{\ 1000}{\text{Molarity}} = 20\text{S cm}^2\text{mol}^{\ 1}$

17. Explain how the phenomenon of adsorption finds application in each of the following processes?

(i) Production of vacuum

(ii) Heterogeneous catalysis

(iii) Froth floatation process

18. Give reasons.

(i) *n*-butyl bromide has higher boiling point than *t*-butyl bromide.

(ii) Racemic mixture is optically inactive.

(iii) The presence of nitro group (¾NO_2) at *o*/*p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

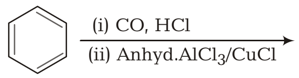
Hint (i) Higher the surface area, higher will be the boiling point of a compound.

(ii) In racemic mixture the two enantiomers rotate the plane-polarised light in opposite directions, the rotations cancel each other because these enantiomers are present in equal amounts.

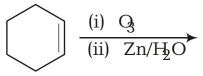
(iii) The reactivity of haloarenes can be increased by the presence of an electron withdrawing group at *o*/*p* positions.

19. Predict the products of the following reactions:

(i)



(ii)



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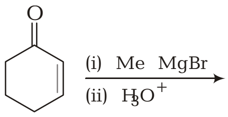
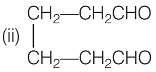


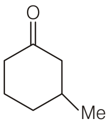
Hint (i) Gattermann-Koch reaction

(ii)



$CH_2—CH_2CHO$ | $CH_2—CH_2CHO$

(iii)



20. How do you convert the followings?

(i) Benzene to phenol

(ii) Ethyl benzene to benzoic acid

(iii) Toluene to methyl benzoate

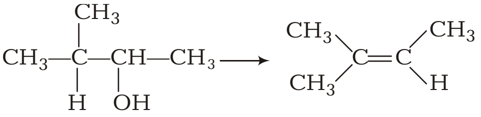
Hint (i) Benzene is sulphonated with oleum and then on acidification gives phenol.

(ii) Oxidation by $KMnO_4$ and alkaline hydrolysis.

(iii) Oxidation followed by esterification.

or

(i) Write the mechanism of the following reaction:



3-methyl-2-butanol 2-methyl-2-butene

Hint (i) ***Step*** **I** Formation of protonated alcohol.

Step **II** Formation of carbocation.

Step **III** Formation of alkene by elimination of a proton.

(ii) Write the mechanism involved in the synthesis of salicylaldehyde from phenol.

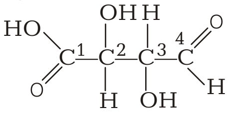
Hint Reimer-Tiemann reaction.

21. (i) Draw the structure of amylopectin.

(ii) Differentiate between a globular protein and a fibrous protein.

(iii) Name the food sources and the deficiency diseases caused due to lack of vitamins A, C, E and K.

22. (i) Which of the carbon-atoms present in the molecule given below are asymmetric.



(ii) Discuss the role of Lewis acid in the preparation of aryl bromide and chlorides in the dark.

(iii) Why iodoform has appreciable antiseptic property?

Hint (i) If a carbon atom satisfies all of its four valencies with four different groups then it is termed as asymmetric/chiral carbon.

(ii) Lewis acids are electron deficient species. They are responsible for inducing heterolytic fission in halogen molecule.

(iii) Antiseptic properties of iodoform is due to the libration of I_2 not because of iodoform itself.

23. Tranquilisers are the drugs which are used for the treatment of stress, mild or even severe mental diseases. These drugs relieve stress, irritability and anxiety by inducing a sense of well being. There are also the essential component of sleeping pills. Now, give the answers of the following questions.

(i) Write the structure of chlorodiazepoxide.

(ii) Why would tranquilisers not been taken regularly for very long period?

(iii) Give an example of tranquilisers used to treat mood changes and depression.

(iv) What values are not possessed by Peoples who commit suicides *via* sleeping pills?

24. (i) Accounts for the following:

(a) Bi(V) is a stronger oxidising agent than Sb(V).

(b) Nitrogen exists as gas whereas phosphorus exists as a solid.

(c) The N¾O bond in NO_2 is shorter than the N¾ O bond in NO_3.

(ii) Draw the structures of the following compounds:.

(a) N_2O_5 (b) Rhombic sulphur.

Hint

(i) (a) Stability of +3 oxidation state increases down the group due to inert pair effect.

(c) Single N¾N bond is weaker than single P¾P bond due to high interelectronic repulsion of the non-bonding electrons, owing to small bond length.

or

(i) Which allotrope of phosphorus is more reactive and why?

(ii) How are the supersonic jet aeroplanes responsible for the depletion of ozone layers?

(iii) F_2 has lower bond dissociation enthalpy than Cl_2. Why?

(iv) Which noble gas is used in filling balloons for meteorological observations?

(v) Complete the equation: $XeF_2 + PF_5$ ¾

Hint

(i) White phosphorus because it is highly unstable molecule.

(ii) $NO(g) + O_3(g)$ ¾ $NO_2(g) + O_2(g)$

(iii) F-atoms has smaller size, while Cl-atoms has comparatively larger in size

(iv) Helium

(v) $XeF_2 + PF_5$ ¾ $[XeF]^+[PF_6]^-$

25. Compound (*X*), containing chlorine, on treatment with strong ammonia gives a solid (*Y*), which is free from chlorine. Composition of (*Y*), upon analysis is found as : C = 49.31%, H = 9.59% and N = 19.18% and reacts with Br_2 and caustic soda to give a basic compound (*Z*). (*Z*) reacts with HNO_2 to given ethanol. Suggest structures for (*X*), (*Y*) and (*Z*).

Hint The molecular formula of '*Y*' is $CH_3CH_2CONH_2$ which undergoes Hofmann bromamide reaction to give $CH_3CH_2NH_2$ (*Z*).

CH_3CH_2COCl on reaction with ammonia give $CH_3CH_2CONH_2$ (*Y*).

or

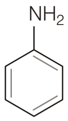
(i) Give one chemical test to distinguish between the following pairs of compound.

(a) Ethylamine and aniline

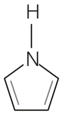
(b) Aniline and N-methyl aniline

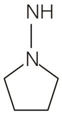
(ii) How will you convert aniline to *o*-bromoaniline?

(iii) Arrange the followings in increasing order of their basic strength.

(a)


(b) NH_3

(c)


(d)


Hint (i) (a) Aniline gives azo dye test while ethylamine does not give this test.

(b) Aniline gives carbylamine test but N-methyl aniline being 2° amine does not give this test.

(ii) ***Step* I** Sulphonation, acetylation.

***Step* II** Bromination (Br_2/CH_3COOH).

***Step* III** Desulphonation.

***Step* IV** Hydrolysis.

26. (i) Dinitrogen pentoxide decomposes according to the following equation,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

This first order reaction was allowed to proceed at 40°C and the data obtained as follows:

$[N_2O_5]$ (mol L^{-1})	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(a) Calculate the rate constant.

(b) What will be the concentration of N_2O_5 after 100 min?

(c) Calculate the initial rate of reaction.

(ii) The decomposition of *A* into product (*P*) has a value of *k* as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation $60\ kJ\ mol^{-1}$. At what temperature would *k* be $1.5 \times 10^4\ s^{-1}$?

Hint

(i) (a) First order reaction, $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = 0.016\ min^{-1}$

(b) $[N_2O_5] = 0.078\ M$

(c) $Rate = k[N_2O_5] = 6.49 \times 10^{-3}\ mol\ L^{-1} s^{-1}$.

(ii) $\log\frac{k_2}{k_1} = \frac{E_a}{2.030R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$; $T_2 = 297K$

or

(i) The decomposition of phosphine, PH_3 proceeds according to the following equation,

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

It is found that the reaction follows the following rate equation, $Rate = k[PH_3]$

The half-life of PH_3 is 37.9 s at 120°C.

(a) How much time is required for 3/4th of PH_3 to decompose?

(b) What fraction of the original sample of PH_3 remains behind after 1 min?

(ii) The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of the activation (E_a) of the reaction assuming that it does not change with temperature ($R = 8.314\ JK^{-1}\ mol^{-1}$, $\log 4 = 0.6021$).

Hint

(i) (a) For first order reaction,

$$k = \frac{0.693}{t_{1/2}}, t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = 75.76\ s$$

(b) $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}, \frac{[R]}{[R]_0} = 0.33$

(ii) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$; $E_a = 52.86 / kJmol^{-1}$

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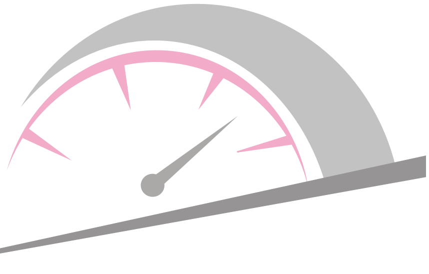


Just Solve & Send

Knowledge Coefficient

Quizzer (No.15)

1. If ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}, how many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?
(a) 3.00 times *(b)* 3.32 times *(c)* 2.50 times (d) 2.90 times

2. Which of the following statements is/are correct?

I. In $SiCl_4$, the central Si-atom has four electrons but it can expand its covalence beyond four due to presence of vacant *d*-orbitals and accept two more Cl^- ions to form $[SiCl_6]^{2-}$.

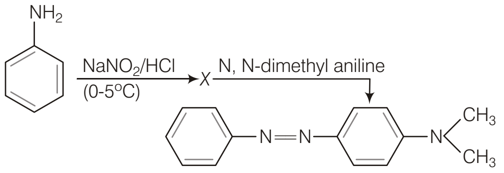
II. On heating, boric acid loses water in three different stages at different temperatures and ultimately give boron trioxide.

III. Duralumin is used to make aircraft body.

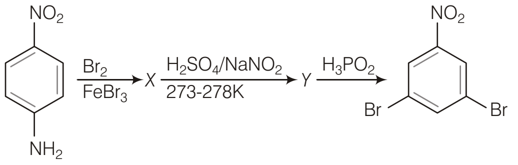
Choose the correct option.
(a) Only I *(b)* II and III *(c)* I and II *(d)* I and III

3. Which of the following reactions is not correct?

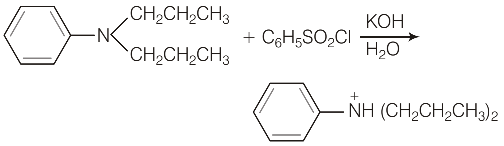
(a)



(b)



(c)



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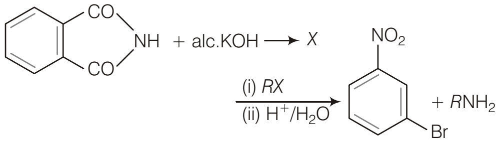


4. Drugstores sell 3% aqueous hydrogen peroxide that is used as an antiseptic. Hydrogen peroxide, H_2O_2 decomposes to water and oxygen. Calculate the volume of oxygen produced if 250 mL of 3% hydrogen peroxide decomposes fully at 750 mm Hg and 22°C.
(a) 3.5 L *(b)* 2.0 L *(c)* 3.0 L *(d)* 4.0 L

5. In muscle cells under the condition of vigorous exercise, glucose is converted to lactic acid, by the chemical reaction given below:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Lactic acid}}{2CH_3CHOHCOOH}; \Delta G^\circ = -197 \text{ kJ}$$

If all of the Gibbs free energy from this reaction was used to convert ADP to ATP, how many moles of ATP could be produced per mole of glucose?
(a) 6.46 *(b)* 4.66
(c) 4.30 *(d)* 6.04

6. Match the following Columns.

Column I (Polymer)		Column II (Use)	
A.	Lucite	p.	Cooking pans coatings
B.	Teflon	q.	Building material insulation
C.	Styrofoam	r.	Indoor-outdoors carpets
D.	Herculon	s.	High quality transparent objects

Codes

	A	B	C	D
(a)	p	s	r	q
(b)	s	p	q	r
(c)	q	r	s	p
(d)	r	q	p	s

7. If enthalpy of vaporisation for chlorofluorocarbon (CCl_2F_2), enthalpy of fusion for solid ice and specific heat capacity for liquid water are 289 J/g, 6.02 kJ/mol and 4.184 $Jg^{-1}C^{-1}$ respectively, what mass of CCl_2F_2 substance must evaporate to freeze 2 moles of water initially at 20°C?
(a) 53.8 g *(b)* 52.7 g
(c) 51.9 g *(d)* 50.3 g

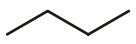
8. Sodium thiosulphate, $Na_2S_2O_3$ is used as a fixer in black and white photography. Assume you have a bottle of sodium thiosulphate and want to determine its purity. The thiosulphate ion can be oxidised with I_2 according to the following reaction,

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

If you use 40.21 mL of 0.246 M I_2 to completely react, a 3.232 g sample of impure $Na_2S_2O_3$, what is the percentage purity of $Na_2S_2O_3$?

(a) 79.2% (b) 70.3%
(c) 69.3% (d) 96.8%

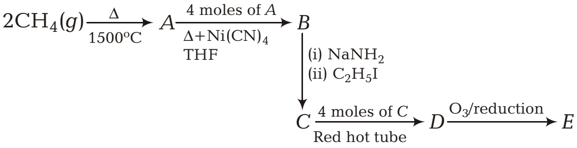
9. 27.8 g mixture of alkyne and alkane (both containing same number of carbon atoms) is dissolved in 1000 g of benzene. The solution freezes at 2.45°C. Another 27.8 g mixture requires 0.6 mole of H_2 for complete hydrogenation. Calculate the chemical formula of alkane (K_f for C_6H_6 = 4.9).

(a)

(b)

(c)

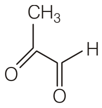
(d)


10. Consider the following reaction,



Find the structure of E.

(a)


(b)


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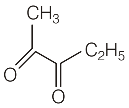

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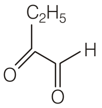

KNOWLEDGE Coefficient

Quizzer (No. 15)

Q. No.	a.	b.	c.	d.	Q. No.	a.	b.	c.	d.
1.	○	○	○	○	6.	○	○	○	○
2.	○	○	○	○	7.	○	○	○	○
3.	○	○	○	○	8.	○	○	○	○
4.	○	○	○	○	9.	○	○	○	○
5.	○	○	○	○	10.	○	○	○	○

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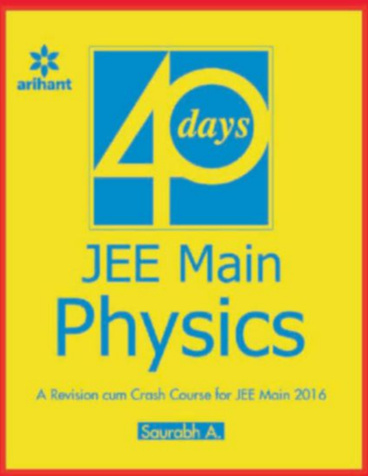

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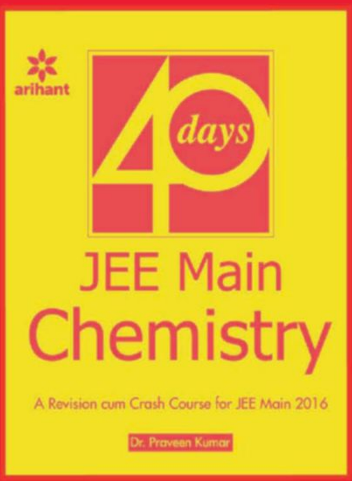

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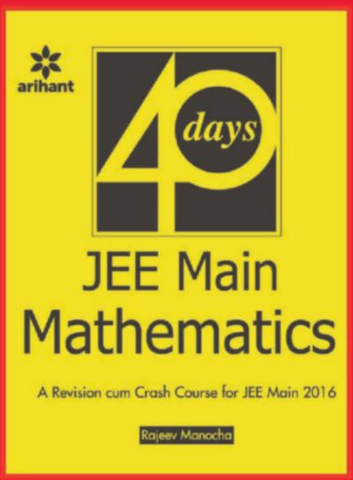

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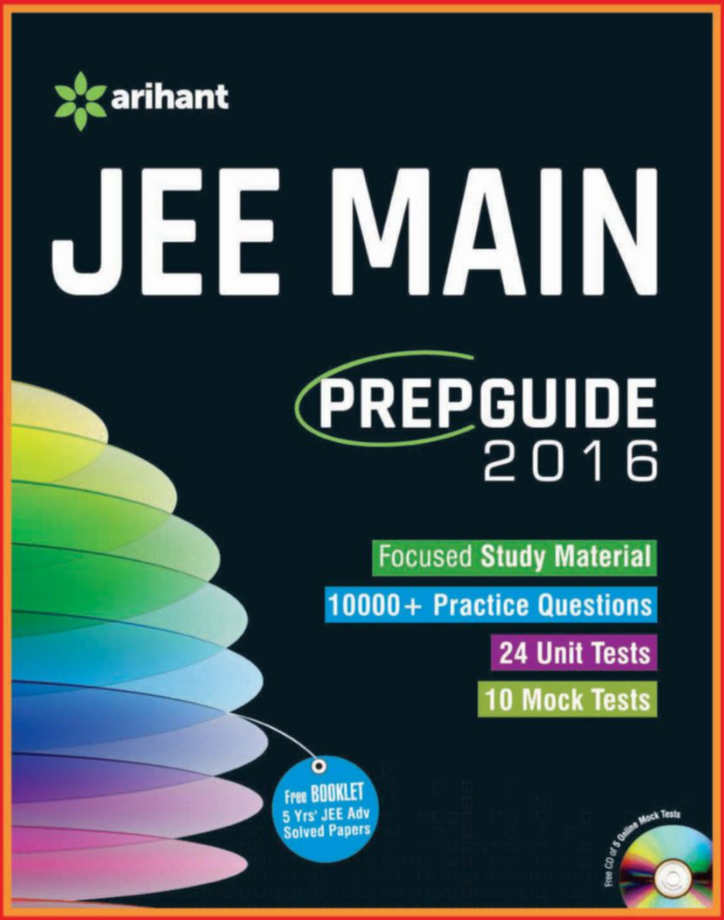

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