September 2016

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## CHEMISTRY CONCENTRATE THE QUANTUM MECHANICAL APPROACH OF BOND FORMATION

METICULOUS ANALYSIS POLARITY AND UNSATURATION : KEY PLAYERS OF CARBONYL COMPOUND'S BEHAVIOUR

CONCEPT MAP ELECTROCHEMISTRY

TOUCH UPS CHEMICAL BONDING ALCOHOLS, PHENOLS AND ETHERS

MEDI MASTER BASH CHEMICAL AND IONIC EQUILIBRIA

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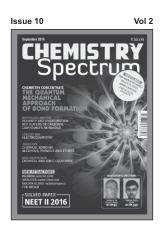
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#### Dear Aspirants,

First of all thanks for your appreciation and feed backs regarding the transformations we did in last issue. Your appreciation always motivates us to put in more efforts for the betterment of spectrum.

Change or Updations are the prime requirements to live in a system with dynamically changing environment. We as Spectrum family also follow the same, and always try to incorporate something new for you. With this ideology we are introducing following new columns from this issue i.e.,

RAINBOW – Section targeted to provide stepwise learning and practice AMPLIFIER – Innovative problems targeted to improve your conceptual learning GOLDEN OLDIES – A collection of best questions from JEE to revise your concepts FUN ARCADE – Specialised section targeted to provide lighter fun based learning Each of these columns is targeted to provide something new, jazzy, and different to develop a deeper insight of the subject. Hope, these columns will prove their worth with a difference and you will like the change. The spectrum team will be anxiously waiting for your feedbacks and comments.

Always 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-

Good luck



#### — MOTIVATOR'S SPECTRUM -

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# JEE TOPPER



#### SCORE CARD

Board: Physics 60, Chemistry 60, Maths 150 JEE Advanced: Maths 108, Physics 96, Chemistry 88

## MESSAGE TO FUTURE ASPIRANTS

Hard work with proper planning, maintaining a cool mind during the exam, giving equal focus to all subjects.

# SUNKESULA SAI PRANEETH REDDY AIR 8<sup>th</sup>

**Q** Achieving top position was a surprise for you or you were expecting it. Praneeth- I was expecting 1 to 10 rank.

**Q** Please share your feeling after achieving such a mile stone. Praneeth- I was very happy and elated.

**Q** In how many attempts did you get this success? Praneeth- First attempt.

**Q** How did you manage to prepare for board examinations and competitive exams simultaneously? Praneeth- Preparing for board exams was very easy, so I didn't spend much time preparing for board exam.

**Q** Please share the secret of your success with our readers. Praneeth- Proper planning while preparing and adopting a proper strategy while writing the exam.

# Q Tell us something about your source of inspiration.

Praneeth- Parents, teachers always encouraged me about my study.

#### Q What was your study plan; please explain in detail so that our readers can also follow it?

Praneeth- Everyday there used to be 6 h of teaching, 6 h of working (2 h for each subject) and 2 h of self study. **Q** Did your study plan remain same throughout the year; at the start of the session, after completion of syllabus and just 1-2 months before the exam or you had different plans for different phases? Praneeth- 2 months before the exam, study plan changed, more focussed on revision.

**Q** How many hours of study, is sufficient for such a success?

Praneeth- 10-12 h is needed, because hard work plays a major role in success.

**Q** Tell us something about your study techniques like how did you memorise the facts, how did you do your revision and how you assessed your preparation from time to time.

Praneeth- To remember facts, I used to write them with seeing once and then without seeing instead of reading them again and again.

**Q** Tell us about your family and the role of your family members in guiding you towards this spectacular performance in the exam.

Praneeth- My family inspired me to join IIT foundation in Viswabharati school, Gudivada (9th, 1oth) 11, 12-Chaina batch.

**Q** Share something about the weak and strong points of your personality. Praneeth- Usually I used to concentrate on what I am doing. I used to feel a little nervous when exams are approached.

**Q** Did you devote equal time to all the subjects or more weightage for one or two subjects as compared to other subjects? Praneeth-I used to feel strong in Physics, so I used to give more time to the other two subjects.

**Q** Were there any weak areas of yours in any subject(s)? How did your cope up with those?

Praneeth- I was weak in maths, which I overcame by guidance from my teachers and more practice.

**Q** How did your teachers/mentors help in achieving this goal?

Praneeth- They used to encourage us whenever we felt difficulty in study.

**Q** Which is your dream institution and which stream do you wish to pursue? Praneeth- IIT Mumbai, CSE.

**Q** Besides studies, what do you do, i.e. what are your hobbies and how do you

match up with these hobbies during your studies? What do you do during the breaks from your studies?

Praneeth- Our college used to arrange things like yoga and indoor games every alternate day.

**Q** Now-a-days social media like Facebook, Twitter etc., is a big trend? Do you also engage with these, does it affect the studies? Please give some advice to our readers.

Praneeth- I didn't involve in social media during these two years.

**Q** Please tell us about the books and other reference material that ensured your success?

Praneeth– Generally, our teachers used to advice about books that are good.

**Q** Did you find Arihant books helping you to get this success?

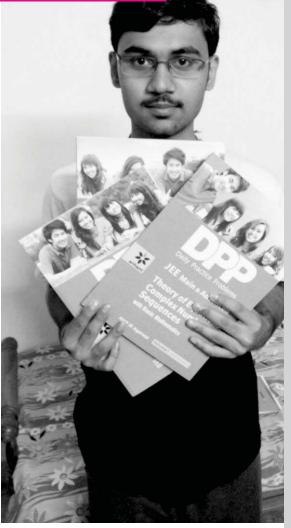
Praneeth– Many books like DC Pandey series, DPP series, spectrum magazine, etc.

## **Q** How Spectrum was helpful in your studies?

Praneeth– Every month new issue helped us to update our study and enhance our knowledge.



# JEE TOPPER



#### SCORE CARD

**Telangana Board:** Physics 140/140, Maths 300/300, Chemistry 136/140, English 191/200, Sanskrit 198/200,

## MESSAGE TO FUTURE ASPIRANTS

Being cool, planning, being systematic is enough. There is no person who failed who followed the above. All the best

# VIGHNESH REDDY AIR 10<sup>th</sup>

# Q Achieving top position was a surprise for you or you were expecting it.

Vighnesh- I was not expecting anything about the result actually, I just concentrated on the topics related. That fetches the result.

## Q Please share your feelings after achieving such a mile stone.

Vighnesh- Its a scholastic experience. But this is not the end, actual battle for life begins after intermediate.

# Q In how many attempts did you get this success?

Vighnesh- In my first attempt. But I practised many exams. In which I failed. I did not get disappointed then. I learned from them.

# Q How did you manage to prepare for board examinations and competitive exams simultaneously?

Vighnesh- For board examinations I started to prepare 2 months before them. Its enough actually.

For competitive exams I was preparing from 9<sup>th</sup> class.

## Q Please share the secret of your success with our readers.

Vighnesh- Plan everything before starting, that's important. Being systematic, learning from mistakes and learning concepts thoroughly all play a great role.

# Q Tell us something about your source of inspiration.

Vighnesh- Actually it was my seniors. I did not follow them but I admired them.

**Q** What was your study plan; please explain in details so that our readers can also follow it?

Vighnesh- Daily I went to my college at 6 : oo AM and returned home at 10 : 30 PM, but it was not hectic. There were many breaks in between on an average 12 h was the time I used to study. For 2-weeks I used to go for break.

Q Did your study plan remain the same throughout the year; at the start of the session, after completion of syllabus and just 1-2 months before the exam or you had different plans for different phases? Vighnesh- In 1st year I completed both Ist and IInd year syllabus. In IInd year I revised again twice.

**Q** How many hours of study, is sufficient for such a success?

Vighnesh- It varies on from person to person. Its sufficient if the individual gets confidence about him but having good practise is necessary for everyone.

**Q** Tell us something about your study techniques like how did you memorise the facts, how did you do your revision and how you assessed your preparation from time to time.

Vighnesh- For memorising (mainly for Inorganic chemistry) I used to practise a lot.

**Q** Tell us about your family and the role of your family members in guiding you towards this spectacular performance in the exam.

Vighnesh- They supported me a lot. They helped me to maintain my health and education.

**Q** Share something about the weak and strong points of your personality. Vighnesh- I did not distinguish between weak and strong. I just did my work and the results came automatically.

**Q** Did you devote equal time to all the subjects or more weightage on one or two subjects as compared to other subjects? Vighnesh-Actually spending equal time is not necessary. It depends how confident you are about a particular subject. On an average I spent more time for Chemistry than Physics and Maths.

**Q** Where there any weak areas of yours in any subject(s)? How did you cope up with those?

Vighnesh-There were few doubtful topics for me. I used to go to my professors and clarify them.

## **Q** How did your teachers/mentors helped in achieving this goal?

Vighnesh- Whenever I had doubt I approached them. They clarified them without any fuss and made me feel that I am good with that topic.

**Q** Which is your dream institution and which stream do you wish to pursue? Vighnesh- IIT Bombay Computer Science Engineering.

**Q** Besides studies, what do you do i.e., what are your hobbies and how you catch up with these hobbies during your studies? What do you do during the breaks from your studies?

Vighnesh- Watching TV, playing badminton.

Q Now-a-days social media like Facebook, Twitter etc; is a big trend. Do you also engage with these, does it affect the studies? Please give some advice to our reader.

Vighnesh- Only during Dusshera and Sankranti Vacations.

**Q** Please tell us the about the books and other reference material that ensured your success.

Vighnesh- Physics : D.C. Pandey, Spectrum magazines.

**Q** Did you find Arihant books helping you to get this success?

Vighnesh-Yes. There were few topics in which I was feeling uncomfortable. I used DPP series to clarify my doubts.

**Q** How Spectrum was helpful in your studies?

Vighnesh- Every month new topics were updated which enhanced my knowledge.





# THE OUANTUM MECHANICAL Approach of Bond Formation

Rakhi Yadav

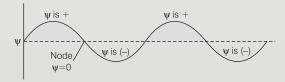
According to quantum mechanical model, we can only predict the probability or relative chance of finding or locating an electron with a probable velocity in a particular region or space around the nucleus. This model was also used to describe detailed electronic nature of chemical bonds. Quantum mechanical model describes the distribution of electrons between two atoms by wave functions.

#### **Wave Function**

The solutions of Schrodinger wave equation are called wave functions, and are represented by Greek letter,  $\psi$ .

#### $\mathbf{Or}$

The wave function,  $\psi$  may be regarded as the amplitude function of a 3D electron wave expressed in terms of *x*, *y* and *z* coordinates.



#### **Characteristics of Wave Function**

- A wave function predicts the allowed energy states of an electron and probability of finding that electron in a given region of space.
- The wave function has no direct physical meaning. However, the square of wave function,  $\psi^2$  is proportional to the probability of finding

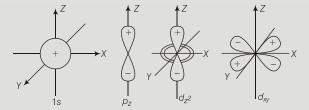
the electron within a small volume of space  $d\tau$ . Thus, in a region where  $\psi^2$  is large, the probability of finding the electron is high and in a region where  $\psi^2$  is small, the probability of finding the electron is low.

•  $\psi^2$  is probability of finding an electron per unit volume in a given region of space and it is termed as probability density.

#### Significance of '+' and '-' Signs Within an Orbital

The shapes of an atomic orbital is dependent on its angular wave function  $Y(\theta, \phi)$ . The angle  $\theta$  or  $\phi$  does not appear in the angular wave function of 1*s*-orbital of hydrogen atom. Thus, electronic distribution remains same throughout the orbital.

• Shapes of some atomic orbitals are shown below.



• The sign shown inside each orbital lobe is the sign of the function  $(\varphi)$  within that region of space. In more simple words we

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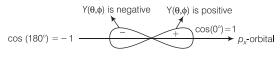
can say that *it* is the sign of the amplitude of a 3D electron wave. Thus, these signs do not have any physical meaning because the electron probability density is given by the square of this function, i.e.  $\phi^2$ .

- Let us take 1s and 2s orbitals. If we start from the nucleus and move away, the 1s orbital always retains the same sign. The 2s orbital passes through a null point and changes sign afterwards.
- The surface on which the 2s-orbital becomes zero is termed as nodal surface. The number of nodal surfaces increases with increasing energy. Thus, 1s-orbital has

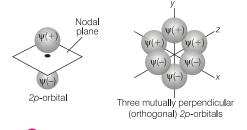


none, 2s-orbital has one and 3s-orbital has two nodal planes.

• For, *p*-orbitals angular wave function depends on  $\cos \theta$ , thus, the boundary surface of *p*-orbitals contains both positive and negative signs.



• A *p*-orbital contains a nodal plane for which  $\psi$  is zero. Any point on the nodal plane has  $\psi = 0$ 



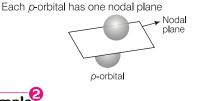
**Example** The number of nodal planes in a  $p_x$ -orbital is [IEE Main 2007]

(a) one (b) two

Sol. (a) Concept Nodal plane is an imaginary plane at which probability of finding an electron is minimum (or zero).

(c) three

(d) zero



**Example** Any *p*-orbital can accommodate upto

(a) four electrons

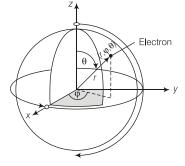
- (b) six electrons
- (c) two electrons with parallel spins
- (d) two electrons with opposite spins
- **Sol.** (d) According to Pauli's exclusion principle, an atomic orbital can accommodate at most two electrons, with opposite spins.

#### **Wave Function In Terms of Angles**

- The distance of electron from the nucleus in terms of polar coordinates shown below.
- An atomic orbital is a mathematical function of three coordinates  $(r, \theta \text{ and } \phi)$  and can be factorised into three separate parts, each of which is a function of only one coordinate.

 $\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$ 

Here, R(r) = radial function and gives the dependence of orbital upon distance 'r' of electron from the nucleus.  $\Theta(\theta)$  and  $\Phi(\phi)$  are angular functions giving the angular dependence of orbital on  $\theta$  and  $\phi$ , respectively.

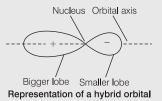


- Angle  $\theta$ , is measured from the positive end of *z*-axis; it's value lies between 0 to  $\pi$ .
- Angle  $\phi$ , is measured counterclockwise along the sphere's equator starting from *x*-axis; it's value lies between 0 to  $2\pi$ .

#### **Hybridisation**

The combining of the wave functions of atomic orbitals of nearly equal energy containing unpaired electron to form new hybrid orbitals of nearly equal energy is called hybridisation.

- The atomic orbitals involved in π-bond formation do not participate in hybridisation due to sidewise overlapping.
- In some cases empty orbitals also participate in hybridisation. Atomic orbitals having lone pair of electrons also participate in hybridisation.
- The electronic charge in hybrid orbitals is concentrated more in one direction, which favours the overlapping of hybrid orbitals. This results in the formation of a larger and a smaller lobe.
- The hybrid orbitals have equivalent energy and identical shape and size. Hence, hybrid orbitals are degenerate.
- The shape of hybrid orbitals are different from that of participating atomic orbitals.



#### CHEMISTRY CONCENTRATE

#### Molecular Orbital Theory (MOT)

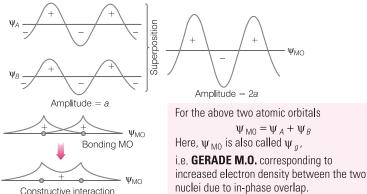
- Valence bond theory (A covalent bond is formed when the orbitals of two atoms containing one unpaired electron each with opposite spins overlaps) and hybrid orbitals observed geometries of molecules in terms of atomic orbitals, but these could not explain all aspects of bonding, e.g. in describing the excited states of molecules, which we must understand to explain how molecules absorb light and give colour.
- Thus, in 1932, Mullikan, Huckel and Hund developed molecular orbital theory of chemical bonding.
- According to this theory, as an atomic orbital is a wave function that describes the distribution of an electron around the nucleus of an atom, so a molecular orbital is a wave function that describes the distribution of an electron over all the nuclei of a molecule. Atomic orbitals with same energy and same symmetry overlap significantly.
- The shapes of molecular orbitals formed depend upon the type of combining atomic orbitals.
- The numbers of molecular orbitals formed are equal to the number of atomic orbitals combined.
- Like atomic orbitals, molecular orbitals have specific energy levels (quantised energy levels) and specific shapes and these orbitals can be occupied by a maximum of two electrons with opposite spins.
- When two atomic orbitals combine, two molecular orbitals are formed one is bonding molecular orbital (BMO) and other is anti-bonding molecular orbital (ABMO).

#### Linear Combination of Atomic Orbitals (LCAO)

To yield qualitative picture of molecular orbitals in a molecule we use a quantum method named as linear combination of atomic orbitals. This method is used because the Schrodinger wave equation is too difficult to apply on the systems containing more than one electron as these electrons are moving in the field of several nuclei. LCAO is a method of superposition of atomic orbitals quantum mechanically as shown below. According to this method wave functions ( $\psi$ ) of individual atomic orbitals linearly combined and form molecular orbitals. Here, two cases can be generated.

#### Formation of Bonding and Anti-bonding Molecular Orbitals by LCAO

**Case I** When two waves are in phase, the waves adds up and constructive interference occurs. The amplitude of new wave is,  $\psi_{MO} = \psi_A + \psi_B$  (Bonding MO).



As probability is given by square of the amplitude.

 $\therefore$  Probability of finding electrons in BMO is,

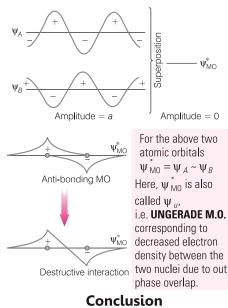
$$\begin{split} \psi_{M0}^2 &= (\psi_A + \psi_B)^2 \\ &= \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B \\ \text{rly} \quad \psi_{M0}^2 &> \psi_A^2 + \psi_B^2 \end{split}$$

clea

Hence, probability of electrons in BMO of molecule is higher than that from individual atomic orbitals.

**Case II** When two waves are out of phase, the wave are subtracted from each others and destructive interference occurs. The amplitude of new wave is

 $\psi^*_{MO} = \psi_A - \psi_B$  (Anti-bonding MO)



Just like the case 1,  $\psi_{M0}^{*2} = (\psi_A - \psi_B)^2$ =  $\psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$  $\psi_{M0}^{*2} < \psi_A^2 + \psi_B^2$ 

Hence, probability of electrons in ABMO of molecule is lower than from individual atomic orbitals.

That means we can say, that BMO has lower energy, hence shows more stability than the corresponding BMO.

First BMO are filled, then ABMO starts filling because BMO has lower energy than that of ABMO.

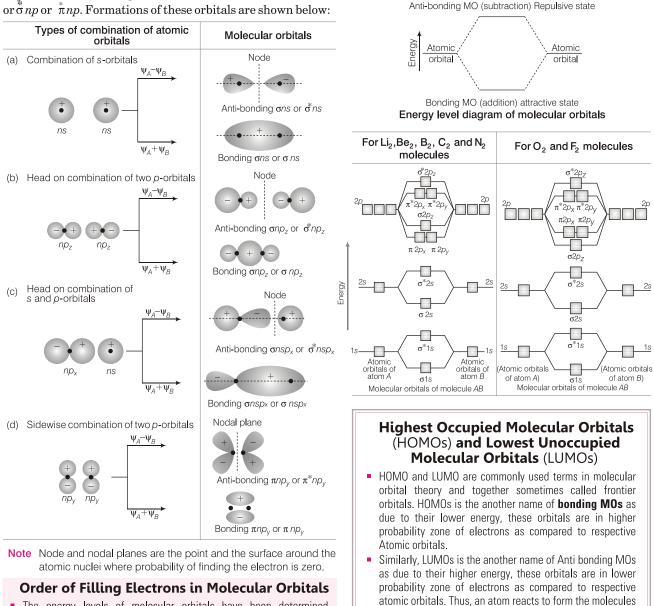


## Sigma ( $\sigma$ ) and Pi ( $\pi$ ) Bonds @ LCAO

The bonding molecular orbitals are shown as  $\sigma ns$  or  $\sigma np$  or  $\pi np$ , while anti-bonding molecular orbitals are shown as  $\sigma ns$  or  $\sigma np$  or  $\pi np$ . Formations of these orbitals are shown below:

#### **Energy Level Diagram of Molecular Orbitals**

The energy level diagram for molecular orbitals is followed as



- The energy levels of molecular orbitals have been determined experimentally from spectroscopic data.
- The molecular orbital with lower energy will be filled first with comparision to the molecular orbital of higher energy.
- The increasing order of energies of molecular orbitals for O<sub>2</sub> and F<sub>2</sub> molecules is given as :

 $\sigma$ 1

$$s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < \pi 2p_x \approx \pi 2p_y$$

$$< \overset{*}{\pi} 2p_{\nu} \approx \overset{*}{\pi} 2p_{\nu} < \overset{*}{\sigma} 2$$

• However, for remaining molecules, i.e.  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$  and  $N_2$  the order is.  $\sigma$  1s <  $\sigma$  1s <  $\sigma$  2s <  $\sigma$  2s <  $\pi$  2 $p_x \approx \pi 2p_y < \sigma 2p_z$ 

 $< \overset{*}{\pi} 2p_{\nu} \approx \overset{*}{\pi} 2p_{\nu} < \overset{*}{\sigma} 2p_{\tau}$ 

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is often related to the nature of the frontier orbitals.

**Applications of Molecular Orbital Theory** 

Here,  $N_b$  = Number of electrons in bonding

 $N_a$  = Number of electrons in anti-bonding

(i) In the calculation of bond order

orbitals.

Bond order =  $\frac{N_b - N_a}{2}$ 

orbitals.

#### CHEMISTRY CONCENTRATE

#### (ii) In the prediction of stability of molecule

- Positive bond order means stable molecule.
- Negative or zero bond order means unstable molecule or you can say that molecule does not exist.
- (iii) In the prediction of number of bonds within the molecule Bond order values 1, 2 and 3 corresponds to single, double and triple bond, respectively.
- (iv) In the prediction of bond length Bond order  $\approx \frac{1}{Bond length}$

As bond order increases bond length decreases. e.g. triple bond has lower value of bond length than double and single bond.

- (v) In the prediction of magnetic nature of molecule
  - (a) If all molecular orbitals are fully occupied, molecule is diamagnetic.
  - (b) If one or more molecular orbitals are singly occupied, substance is paramagnetic.
- Note There is evidence from ultraviolet photoelectron spectroscopy to suggest that hybridisation is not real. There is more advanced theory of bonding called molecular orbital theory, but this is much complicated and does not allow us to draw lines (bonds) between atoms.

**Example**<sup>S</sup> The total number of electrons that take part in forming the bonds in  $N_2$  is

(a) 2 (b) 4 (c) 6 (d) 10

**Sol.** (c) Total number of electrons in  $N_2 = 14$ 

:. Filling of molecular orbitals follows the order

$$\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2 < \pi 2p_x^2 \approx \pi 2p_y^2 < \sigma 2p_z^2$$
  
$$\therefore \text{ Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

 $N_2$  has bond order 3. Thus, it has three covalent bonds. Each covalent bond is associated with two electrons. Hence, six electrons are involved in forming bonds in  $N_2.$ 

Example

Stability of the species  $\mathrm{Li}_2,\,\mathrm{Li}_2^-$  and  $\mathrm{Li}_2^+$  increases

in the order of

[JEE Main 2013]

(a) $Li_2 < Li_2^+ < Li_2^-$	(b) $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$
(c) $Li_2 < Li_2^- < Li_2^+$	(d) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$

#### Sol. (b) Thinking process

- (i) Stability of an species decreases as bond order decreases.
- (ii) If bond order is same for two different species then the species which has more number of electrons in anti-bonding orbitals will be least stable.

For Li<sub>2</sub>(3 + 3 = 6e<sup>-</sup>s) = 
$$\sigma 1s^2$$
,  $\overset{*}{\sigma} 1s^2$ ,  $\sigma 2s^2$   
Bond order =  $\frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$   
For Li<sub>2</sub><sup>+</sup> (3 + 3 - 1 = 5e<sup>-</sup>s) =  $\sigma 1s^2$ ,  $\sigma^* 1s^2$ ,  $\sigma 2s^1$   
Bond order =  $\frac{3 - 2}{2} = 0.5$ 

For 
$$\text{Li}_{2}^{-}(3+3+1=7e^{-}s)$$
  
=  $\sigma 1s^{2}$ ,  $\sigma 1s^{2}$ ,  $\sigma 2s^{2}$ ,  $\sigma 2s^{1}$   
Bond order =  $\frac{4-3}{2} = 0.5$   
 $\therefore$  Stability order is  $\text{Li}_{2} < \text{Li}_{2}^{+} < \text{Li}_{2}$ 

Example According to MO theory,

[2008, 1M]

- (a)  $\mathsf{O}_2^+$  is paramagnetic and bond order is greater than  $\mathsf{O}_2$
- (b)  $O_2^+$  is paramagnetic and bond order is less than  $O_2^-$
- (c)  $O_2^+$  is diamagnetic and bond order is less than  $O_2^-$

(d)  $\mathrm{O}_2^+$  is diamagnetic and bond order is more than  $\mathrm{O}_2$ 

**Sol.** (a) 
$$O_2^+(15e^-)$$
:  $\sigma 1s^2$ ,  $\hat{\sigma} 1s^2 \sigma 2s^2$ ,  $\sigma^* 2s^2 \sigma 2p_z^2$ 

$$\pi 2 p_x^2 \approx \pi 2 p_y^2, \ \hat{\pi}^2 p_x^1 \approx \pi^* 2 p_y^0$$
  
Bond order =  $\frac{10-5}{2}$  = 2.5 ; paramagnetic  
O<sub>2</sub> (16e<sup>-</sup>) :  $\sigma 1s^2, \ \sigma^1 1s^2, \ \sigma 2s^2, \ \sigma^* 2s^2$   
 $\sigma 2 p_z^2 \ \pi 2 p_x^2 \approx \pi 2 p_y^2, \ \pi^* 2 p_x^1 \approx \pi^* 2 p_y^1$   
Bond order =  $\frac{10-6}{2}$  = 2

Hence,  $O_2^+$  is paramagnetic and bond order is greater than  $O_2$ .

**Example** In which of the following pairs of molecules/ions both the species are not likely to exist?

(a) H<sub>2</sub><sup>+</sup>, He<sub>2</sub><sup>2-</sup>
 (b) H<sub>2</sub><sup>-</sup>, He<sub>2</sub><sup>2-</sup>
 (c) H<sub>2</sub><sup>2+</sup>, He<sub>2</sub>
 (d) H<sub>2</sub><sup>-</sup>, He<sub>2</sub><sup>2+</sup>
 Sol. (c) Species that have zero or negative bond order do not exist.

$$H_2^{2+}$$
 (1 + 1 - 2 = 0) =  $\sigma 1 s^0$ 

Bond order = 0

Bo

He<sub>2</sub>(2 + 2 = 4e<sup>-</sup>s) = 
$$\sigma 1s^2, \dot{\sigma} 1s$$
  
nd order =  $\frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$   
H<sup>2+</sup> and He<sub>2</sub> do not exist

So,  $H_2^{2+}$  and  $He_2$  do not exist.

**Example** Assuming Hund's rule is violated, the bond order of the diatomic molecule B<sub>2</sub> is.

$$\sigma_{1s}, \overset{*}{\sigma}_{1s}, \sigma_{2s}, \overset{*}{\sigma}_{2s} \left[ \begin{matrix} \pi 2 \rho_{x} \\ \pi 2 \rho_{y} \end{matrix} \right], \sigma_{2s}^{2} \sigma_{2s}^{2} \left[ \begin{matrix} \pi 2 \rho_{x} \\ \pi 2 \rho_{x} \\ \pi 2 \rho_{y} \end{matrix} \right]$$

For B<sub>2</sub>

Total number of electrons = 10

Molecular orbital electronic configuration is given as,

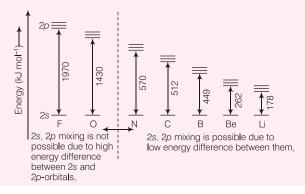
$$\sigma 1s^{2}, \ \overset{*}{\sigma} 1s^{2}, \ \sigma 2s^{2}, \ \overset{*}{\sigma} 2s^{2}, \left[\frac{\pi 2 p_{x}^{1}}{\pi 2 p_{y}^{1}}\right]$$
  
. Bond order =  $\frac{N_{b} - N_{a}}{2} = \frac{6 - 4}{2} = 1$ 

#### 10 > SEPTEMBER 2016 >> CHEMISTRY SPECTRUM

#### CHEMISTRY CONCENTRATE

#### s-p MIXING

- *s*-*p* mixing refers to the interactions between MOs with compatible symmetry that result from the combination of 2 s and  $2 p_z$  valence atomic orbitals with comparable energies.
- The *s*-*p* mixing of MOs is different from the concept of hybridisation of AOs of comparable energies within the same atom.
- In case of  $F_2$  and  $O_2$ , we assume that the interactions between the s-orbitals and interactions among p-orbitals are completely independent because of large energy gap between 2s and 2p-orbitals.
- But in case of  $B_2$ ,  $C_2$  and  $N_2$  energy gap between 2s and 2p -orbitals is not large. Hence, these orbitals interact with each other and this effect is known as s-p mixing.
- · Generally, orbitals of same symmetry interact with each other. This means  $2\sigma_a$  orbitals (derived from 2s-orbitals) interact with the  $3\sigma_a$  orbitals (derived from  $2p_z$  orbitals).
- Similarly  $2\sigma_{\mu}$ -orbitals interact with each other.
- s-p mixing leads to stabilisation of  $2\sigma_q$  and  $2\sigma_u^*$ -orbitals and destabilisation of the  $3\sigma_a$ -orbitals as they pushes  $3\sigma_a$ -orbitals above  $1\pi_{\mu}$ -orbitals (derived from  $2p_x$  and  $2p_y$  orbitals) in energy level. The  $\pi$ -orbitals are not affected by *s*-*p* mixing as these are of wrong symmetry to interact with the *s*-based  $\sigma$ -orbitals.
- The following diagram shows the difference in the energies of 2s and  $2p_{z}$  atomic orbitals of atoms of second row elements.



Example Assuming 2s-2p mixing is not operative, the paramagnetic species among the following is

> [JEE Advanced 2014]  $(d) N_2$

(a) Be<sub>2</sub>  $(b) B_2$ Sol. (c) Thinking process

• As there is no 2s-2p mixing so apply the molecular orbital electronic configuration of without s-p mixing to all the given species.

(c) C<sub>2</sub>

• Find out the species which contains unpaired electrons. Assuming that there is no 2s-2p mixing takes place the molecular orbital electronic configuration can be written in the following sequence of energy levels of molecular orbitals.

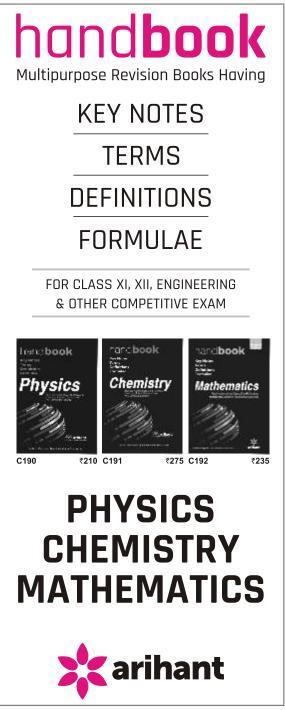
$$\sigma_{1s} < \sigma_{1s} < \sigma_{2s} < \sigma_{2s} < \sigma_{2s} < \sigma_{2p_z} < \pi_{2p_x} \equiv \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y} < \sigma_{2p_z}^*$$
$$\equiv \pi_{2py}^* < \sigma_{2p_z}^*$$

(a) 
$$Be_2(8e) \to \sigma 1s^2, \sigma 1s^2, \sigma 2s^2, \sigma 2s^2, \sigma 2s^2$$
  
(b)  $B_2(10\bar{e}) \to \sigma 1s^2, \sigma 1s^2, \sigma 2s^2, \sigma 2s^2, \sigma 2p_z^2, \pi 2p_v^0, \pi 2p_v^0$ 

(c)  $C_2(12\bar{e}) \rightarrow \sigma 1s^2$ ,  $\overset{*}{\sigma} 1s^2$ ,  $\sigma 2s^2$ ,  $\sigma^* 2s^2 \sigma 2p_z^2$ ,  $\pi^2 p_x^{\downarrow}$ ,  $\pi_2^2 p_x^{\downarrow}$  $\pi 2 \rho_v^1, \pi 2 \rho_v^0$ 

(d)  $N_2(14\bar{e}) \rightarrow \sigma_1 s^2, \overset{*}{\sigma}_1 s^2, \sigma_2 s^2, \sigma_2 s^2, \sigma_2 \rho_z^2, \pi^2 \rho_x^2, \pi^* 2\rho_x^0$  $\pi 2 p_v^2, \pi^* 2 p_v^0$ 

Among all the given species only C2 has unpaired electron, thus, it is paramagnetic species.



#### **Schematic Properties of Diatomic Molecules**

Ν

#### Valence Electron Configuration

 $B_2 = (\sigma 2s)^2 (\overset{*}{\sigma} 2s)^2, (\pi 2p)^2,$  $C = \frac{1}{2} \left( \frac{1}{2} \right)^{2} \left( \frac{1}{2} \right)^{2} \left( \frac{1}{2} \right)^{4}$ 

$$U_2 = (\sigma_{2s})^{-} (\sigma_{2s})^{-} (\pi_{2p})^{-}$$

 $N_2 = (\sigma 2s)^2 (\sigma^2 2s)^2 (\pi 2p)^4, (\sigma 2p)^2$  $O_2 = (\sigma 2s)^2 (\overset{*}{\sigma} 2s)^2 (\sigma 2p)^2 (\pi 2p)^4 (\overset{*}{\pi} 2p)^2$ 

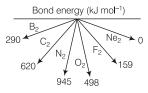
$$F_{2} = (\sigma 2s)^{2} (\overset{\circ}{\sigma} 2s)^{2} (\sigma 2p)^{2} (\pi 2p)^{4} (\overset{\circ}{\pi} 2p)^{4}$$

Ne<sub>2</sub> =  $(\sigma 2s)^2$ ,  $(\overset{*}{\sigma} 2s)^2$ ,  $(\sigma 2p)^2$ ,  $(\pi 2p)^4$ ,  $(\overset{*}{\pi} 2p)^4$ ,  $(\overset{*}{\sigma} 2p)^2$ 

#### **Magnetic Properties**

- The species which has unpaired electrons, shows paramagnetic behaviour (when, it gets attracted to an external magnetic field) while the species which has paired electrons, shows diamagnetic behaviour (It does not get attracted towards applied external magnetic field).
- B<sub>2</sub>, O<sub>2</sub> are paramagnetic while C<sub>2</sub>, N<sub>2</sub> and F<sub>2</sub> are diamagnetic in nature.

#### **Bond Energy**



- Bond energy is directly proportional to bond order, i.e. as bond order increases, bond energy also increases.
- N<sub>2</sub>, shows maximum bond energy, i.e. it requires maximum bond energy in order to break its bond as its bond order is maximum (3).
- $C_2$  and  $O_2$  both have same bond order but,  $O_2$  requires less energy to break its bond because it has unpaired electrons in its outermost molecular orbital. Ne2, has zero bond energy as there is no bond between Ne atom.

	Wit	n 2s <b>-</b> 2p mixi	ng	Without 2s-2p mixing			]
	B <sub>2</sub>	C <sub>2</sub>	$N_2$	O <sub>2</sub>	$F_2$	Ne <sub>2</sub>	]
$\sigma_{2\rho}^{*}$						$\uparrow\downarrow$	$\sigma_{2\rho}^{\star}$
$\pi_{2p}^{*}$				$\uparrow \uparrow$	$\uparrow\downarrow\uparrow\downarrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	π <sub>2ρ</sub>
$\sigma_{2p}$			$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	π <sub>2ρ</sub>
$\pi_{2p}$	$\uparrow\uparrow\uparrow$	$\uparrow\downarrow\uparrow\downarrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ <sub>2p</sub>
$\sigma_{\text{2s}}^{*}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\sigma_{2s}^{*}$
$\sigma_{2s}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\sigma_{2s}$

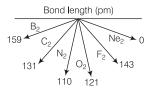
#### **Bond Order**

Bond order = 
$$\frac{N_b - N_a}{2}$$

$$B_2 = \frac{4-2}{1} = 1$$
,  $O_2 = \frac{8-4}{2} = 2$ ,  $C_2 = \frac{6-2}{2} = 2$ ,  $F_2 = \frac{8-6}{2} = 1$ ,  
 $N_2 = \frac{8-2}{2} = 3$ ,  $Ne_2 = \frac{8-8}{2} = 0$ 

As, bond order is zero in case of Ne<sub>2</sub> so, no bond formation takes place between Ne atoms.

#### **Bond Length**



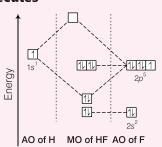
- Bond length decreases as bond order increases. Thus, bond length of Ne<sub>2</sub> is zero because its bond order is also zero.
- $B_2$  and  $F_2$  have maximum bond lengths among all. But  $F_2$  has smaller bond length than B2 molecule. It is due to maximum electronegativity of F-atom. F-atoms bind their shared electrons more tightly than B-atoms.
- N<sub>2</sub> shows minimum bond length among all as it has maximum bond order, i.e. 3.

#### Formation and Stability of Heteronuclear Molecules

As the energies of input atomic orbitals will not be same, which will give rise to unequal splitting of MO's. Bonding orbitals will have more character of stable AO while anti-bonding orbitals will have more character of unstable combining AO. Only AO' of comparable energies can be combined to form MO's.

#### Facts

- 1s-orbital of H is too high in energy that it cannot interact with 1s or 2s orbital of fluorine.
- It interacts only with one 2p-orbital having similar symmetry to form MO's indicated in the figure.
- Out of total 8 valence electrons of HF molecule, only two are in delocalised MO's.



# Smart Practice

- **1.** Which of the following molecule or ion is unstable? (a)  $\operatorname{He}_2$  (b)  $\operatorname{He}_2^-$  (c)  $\operatorname{He}_2^+$  (d)  $\operatorname{H}_2^-$
- 2. Which of the following molecule represents bond order equals to 3?

 $(a) \, {\rm H}_2 \qquad (b) \, {\rm C}_2 \qquad (c) \, {\rm N}_2 \qquad (d) \, {\rm O}_2$ 

- Which among the following molecules/ions is diamagnetic?
   (a) Super oxide ion
  - (b) Oxygen
  - (c) Carbon molecule
  - (d) Unipositive ion of  $N_2$  molecule
- 4. The molecule having highest bond energy is (a) N—N (b) F—F (c) C—C (d) O—O

**Hint** Bond energy of a single bond increases as we go along the given period. But still C—C bond energy is greatest because electron-electron repulsion is very high in N—N, O—O and F—F due to small size of atoms weakening their respective bonds.

- **5.** The common features for the species CN<sup>-</sup>, CO, NO<sup>+</sup> and N<sub>2</sub> are
  - (a) isoelectronic, paramagnetic, bond order three  $% \left( a\right) =\left( a\right) \left( a\right) \left$
  - (b) isoelectronic, diamagnetic, bond order three  $% \left( b\right) =\left( b\right) \left( b\right) \left($
  - (c) isoelectronic, paramagnetic, bond order two
  - $\left( d\right)$  isoelectronic, diamagnetic, bond order two
- **6.** According to MO theory which of the following lists ranks of nitrogen species in terms of increasing bond order?

$$\begin{aligned} &(a)\,\bar{\mathbf{N}}_2\,<\,\mathbf{N}_2\,<\,\mathbf{N}_2^{2-} &(b)\,\mathbf{N}_2^{2-}\,<\,\mathbf{N}_2^{-} <\mathbf{N}_2 \\ &(c)\,\mathbf{N}_2\,<\,\mathbf{N}_2^{2-}\,<\,\mathbf{N}_2^{-} &(d)\,\mathbf{N}_2^{-}\,<\,\mathbf{N}_2^{2-}\,<\,\mathbf{N}_2 \end{aligned}$$

7. Which of the following diatomic molecules would be stabilised by the removal of an electron?

 $(a) \operatorname{C}_2 \qquad (b) \operatorname{CN} \qquad (c) \operatorname{N}_2 \qquad (d) \operatorname{O}_2$ 

**Hint** A molecule is stabilised if bond order increases and an anti-bonding electron is lost.

- 8. If one of the electrons of helium is taken in excited state then bond order of He<sub>2</sub> is (a) 0 (b) 1 (c) 0.5 (d) 2.0
- 9. If the bond energy of  $H_2$  is 436 kJ mol<sup>-1</sup>, bond energy of  $H_2^+$  is

(a) $436 \text{ kJ mol}^{-1}$	(b) 218 kJ mol $^{-1}$
(c) $327 \text{ kJ mol}^{-1}$	$(d) 872 \text{ kJ mol}^{-1}$

**Hint** Bond energy of  $H_2^+$  = Bond order × Bond energy of one H—H bond.

**10.** The species having bond order different from that in CO is

(a) NO <sup>-</sup>	(b) NO <sup>+</sup>
$(c) \operatorname{CN}^{-}$	$(d)$ N $_2$

**11.** Increasing order of bond strength of  $O_2$ ,  $O_2^-$ ,  $O_2^{-2}$  and  $O_2^+$  is

 $\begin{array}{l} (a) \ O_2^+ < O_2 < O_2^- < O_2^{2-} \\ (b) \ O_2 < O_2^+ < O_2^- < O_2^{2-} \\ (c) \ O_2^- < O_2^{2-} < O_2^+ < O_2 \\ \end{array} (b) \ O_2^{2-} < O_2^- < O_2^{2-} < O_2^+ \\ \end{array}$ 

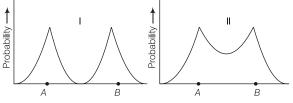
- 12. The bond order in NO is 2.5 while that in NO<sup>+</sup> is 3. Which of the following statements is true for these two species?
  - (a) Bond angle in NO<sup>+</sup> is greater than in NO
  - (b) Bond length in NO is greater than in NO<sup>+</sup>
  - (c) Bond length in NO $^+$  is equal to that in NO
  - (d) Bond length is unpredictable
- **13.** Which of the following molecules/ions does not contain unpaired electrons? (a)  $O_2^{2-}$  (b)  $B_2$  (c)  $N_2^+$  (d)  $O_2$
- 14. Which one of the following pairs of species have the same bond order?
  (a) CN<sup>-</sup> and NO<sup>+</sup>
  (b) CN<sup>-</sup> and CN<sup>+</sup>
  (c) O<sub>2</sub><sup>-</sup> and CN<sup>-</sup>
  (d) NO<sup>+</sup> and CN<sup>+</sup>
- **15.** Which one of the following constitutes a group of isoelectronic species?

 $\begin{array}{ll} (a) \, \mathrm{C}_2^{2-}, \, \mathrm{O}_2^{-}, \, \mathrm{CO}, \, \mathrm{NO} & (b) \, \mathrm{NO}^+, \, \mathrm{C}_2^{2-}, \, \mathrm{CN}^-, \, \mathrm{N}_2 \\ (c) \, \mathrm{CN}^-, \, \mathrm{N}_2, \, \mathrm{O}_2^{2-}, \, \mathrm{CO}_2^{2-} & (d) \, \mathrm{N}_2, \, \mathrm{O}_2^-, \, \mathrm{NO}^+, \, \mathrm{CO} \end{array}$ 

- 16. Which of the following statements is incorrect about MO theory?
  - (a) Molecular orbital is a wavefunction that describes the distribution of an electron overall the nuclei of a molecule
  - (b) Atomic orbitals with different energy and same symmetry overlap significantly
  - (c) The shapes of molecular orbitals formed depend upon the type of combining atomic orbitals
  - $\left( d\right)$  The numbers of molecular orbitals are fomed equal to the number of atomic orbitals combined

**17.** 
$$H_A + H_B \longrightarrow H_2$$
 ( $\sigma$ -bond)

Probability (electron charge density) of bonding and anti-bonding molecular orbitals are given in the following figures.



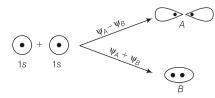
Select the correct probability. (a) I bonding, II anti-bonding (b) II bonding, I anti-bonding (c) Both I and II are bonding

(d)Both I and II are anti-bonding

Prob

#### 🔁 CHEMISTRY CONCENTRATE

**18.** Consider the following figure,



Here, A and B refer to

A	B
$(a) \sigma 1s$	$\sigma^* 1 s$
(b) $\sigma^* 1s$	$\sigma 1s$
$(c) \sigma 1s$	$\sigma \ 1s$
$(d) \sigma^* 1s$	$\sigma^* 1 s$

- **19.** Which of the following statements are incorrect about wave function?
  - (a) A wave function predicts the allowed energy states of an electron
  - (b) The square of wave function is the probability of finding an electron in a given region of space
  - (c) The wave function does not have a direct physical meaning
  - (d) All the above are incorrect

**20.** Which of the following statements is not correct?

- (a)  $F_2^+$  has a higher bond order than  $F_2$
- (b)  $O_2^+$  has a higher bond order than  $O_2^-$
- (c)  $N_2^-$  has a lower bond order than  $O_2$
- (d) NO<sup>+</sup> has a lower bond order than NO
- **21.** Concept of bond order in the molecular orbital theory depends on the number of electrons in the bonding and anti-bonding orbitals. The bond order (a) is a non-zero quantity
  - (b) can be any positive value, including zero
  - (c) can have a negative value
  - (d) has always an integral value
- **22.** The cyanide ion,  $CN^-$  and  $N_2$  are isoelectronic species, but in contrast to  $CN^-$ ,  $N_2$  is chemically inert, because of
  - (a) low bond energy
  - (b) absence of polarity
  - (c) unsymmetrical electron distribution

(d) presence of more electrons in bonding orbitals

- **23.**  $N_2$  and  $O_2$  are converted into monocations. Which of the following statements are wrong? (a)  $In O_2$ , paramagnetism decreases (b) N<sup>+</sup><sub>2</sub> becomes diamagnetic (c) In N  $_{\rm 2},$  the N—N bond is weaker (d) In O  $_2$ , the O — O bond order increases
- **24.** Which of the following statements is not correct from the view point of molecular orbital theory?
  - (a)  $\operatorname{Be}_2$  is not a stable molecule
  - (b)  $\operatorname{He}_2$  is not stable but  $\operatorname{He}_2^+$  is expected to exist
  - (c) Bond strength of  $N_2$  is maximum amongst the homonuclear diatomic molecules belonging to the second period
  - (d) The order of energies of molecular orbitals in  $N_2$ molecule is  $\sigma 2s < \sigma^2 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y)$

 $<(\pi^*2\rho_x = \pi^*2\rho_y) < \sigma^*2\rho_z$ 

**25.** Which of the following molecular orbitals has two nodal planes?

$$\sigma 2p_x$$
 (b)  $\pi 2p_y$  (c)  $\pi 2p_y$  (d)  $\sigma 2p_x$ 

- **26.** In which of the following diatomic molecules /ions is the bond order of each molecule/ion = 2.5? (a) O<sup>+</sup><sub>2</sub>, NO, CN<sup>-</sup>  $(b) CN^{-}, N_{2}^{+}, N_{2}$ (c)  $N_2^+$ , NO,  $O_2^+$  $(d) O_2^+, CN^-, N_2^+$
- **27.** In the formation of  $NO^+$  from NO, the electron is removed from a (b)  $\pi$ -orbital (a)  $\sigma$ -orbital (c)  $\sigma^*$ -orbital
- **28.** The HOMO in CO is (b)  $\pi$ -anti-bonding (a)  $\pi$ -bonding (c)  $\sigma$ -anti-bonding (d)  $\sigma$ -bonding
- **29.** According to linear combination of atomic orbitals of atoms A and B which relation is true.  $\begin{array}{ll} (a) \left(\psi_{\rm MO}^*\right)^2 < \psi_A^2 + \psi_B^2 & (b) \left(\psi_{\rm MO}^*\right)^2 < \psi_A^2 - \psi_B^2 \\ (c) \left(\psi_{\rm MO}\right)^2 = \left(\psi_A - \psi_B\right)^2 & (d) \left(\psi_{\rm MO}\right)^2 < \psi_A^2 - \psi_B^2 \end{array}$
- **30.** The relative stability of  $H_2$ ,  $H_2^+$  and  $H_2^-$  is in the order
  - $(a) H_2^+ > H_2^- < H_2$  $(b)\,{\rm H}_2^- < {\rm H}_2^+ < {\rm H}_2$  $(c)\,{\rm H}_2^+\,<{\rm H}_2\,<{\rm H}_2^-$

(a)

(d) H<sub>2</sub> < H<sub>2</sub><sup>-</sup> < H<sub>2</sub><sup>+</sup>

#### Answers

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



Lipstick goes all the way back to 60 B.C when Cleopatra had her lipstick made from crushed carmine beetles and ants for a base which gave a deep red pigment. Today the most common materials used to make lipstick are Beeswax (Pigment) and Castor oil (Shiny Film), although some recent brands have begun to use Silicon based Alkenes such as Silicon Polyethylene.

(d)  $\pi^*$ -orbital



# **NEET 2016** (PHASE II)

# SOLVED PAPER

A COLLECTION OF ASSORTED SOLVED KNOCK OUTS

#### -INSTRUCTIONS -

Held on 24-7-2016

- This test consists of 45 questions.
- Each question carries 4 marks for correct response.
- For each incorrect response, one mark will be deducted form the total scores.
- No deduction from the total score will be made if no response is indicated for question in the answer sheet.
- There is only one correct option for each question. Filling up more than one response in any question will be treated as wrong response and mark for wrong response will be deducted according as per instructions.

## **EXAM CRUX**

- In Chemistry Section, most of the questions in NEET Phase-II question paper were theoretical, i.e. concept based. Out of total 45 questions, only 7 questions were numericals directly based on formula or calculation. Out of conceptual questions, some were tricky while some others (4) were beyond the scope of NCERT. The question paper was slightly unbalanced with 17 questions were related to class 11th syllabus and rest 38 to class 12th syllabus.
- From difficulty level point of view approximately 40% questions were easy (*E*), 51% were relatively moderate (*M*) and remaining questions were difficult (*D*) in nature. There was also a question with 2 correct answers.

#### By Arihant Team

- Which one of the following compounds shows the presence of intramolecular hydrogen bond? [Chemical Bonding, E]
   (a) H<sub>2</sub>O<sub>2</sub>
   (b) HCN
   (c) Cellulose
   (d) Concentrated acetic acid
  - (c) Centrose (a) Concentrated acetic acid
- 2. The molar conductivity of a 0.5 mol/dm<sup>3</sup> solution of AgNO<sub>3</sub> with electrolytic conductivity of  $5.76 \times 10^{-3}$  S cm<sup>-1</sup> at 298 K is [Electrochemistry, E] (a) 2.88 S cm<sup>2</sup>/mol (b) 11.52 S cm<sup>2</sup>/mol (c) 0.086 S cm<sup>2</sup>/mol (d) 28.8 S cm<sup>2</sup>/mol

- **3.** The decomposition of phosphine (PH<sub>3</sub>) on tungsten at low pressure is a first-order reaction. It is because the [Chemical Kinetics, M]
  - (a) rate is proportional to the surface coverage
  - (b) rate is inversely proportional to the surface coverage
  - (c) rate is independent of the surface coverage
  - (d) rate of decomposition is very slow
- **4.** The coagulation values in millimoles per litre of the electrolytes used for the coagulation of  $As_2S_3$  are given below [Surface Chemistry, M]
  - $\begin{array}{ll} \mathrm{I.} \ (\mathrm{NaCl}) = 52 & \mathrm{II.} \ (\mathrm{BaCl}_2) = 0.69 \\ \mathrm{III.} \ (\mathrm{MgSO}_4) = 0.22 \\ \mathrm{The \ correct \ order \ of \ their \ coagulating \ power \ is} \\ (a) \ \mathrm{I} > \mathrm{II} > \mathrm{III} & (b) \ \mathrm{II} > \mathrm{I} > \mathrm{III} \\ (c) \ \mathrm{III} > \mathrm{II} > \mathrm{I} & (d) \ \mathrm{III} > \mathrm{II} > \mathrm{II} \\ \end{array}$
- 5. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mole of chlorine gas using a current of 3 amperes is [Electrochemistry, D]
  (a) 55 min
  (b) 110 min
  (c) 220 min
  (d) 330 min
- 6. How many electrons can fit in the orbital for which n = 3 and l = 1? [Atomic Structure, M] (a) 2 (b) 6 (c) 10 (d) 14

#### 🔁 EXAM SPECTRUM

7. For a sample of perfect gas when its pressure is changed isothermally from  $p_i$  to  $p_f$ , the entropy change is given by [Thermodynamics, M]

(a) 
$$\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$$
  
(b)  $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$   
(c)  $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$   
(d)  $\Delta S = RT \ln\left(\frac{p_f}{p_f}\right)$ 

**8.** The van't Hoff factor (*i*) for a dilute aqueous solution of the strong electrolyte barium hydroxide is Solutions, MI

$$(a) 0 (b) 1 (c) 2 (d) 3$$

**9.** The percentage of pyridine  $(C_5H_5N)$  that forms pyridinium ion  $(C_5H_5N^+H)$  in a 0.10 M aqueous pyridine solution ( $K_{\rm b}$  for  $C_5H_5N = 1.7 \times 10^{-9}$ ) is [Solutions, M]

(c) 0.77% (a) 0.0060%*(b)* 0.013% (d) 1.6%

- **10.** In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca<sup>2+</sup>) and fluoride ion (F<sup>-</sup>) are [Solid State, M] (a) 4 and 2 (b) 6 and 6 (c) 8 and 4 (d) 4 and 8
- **11.** If the  $E_{cell}^{\circ}$  for a given reaction has a negative value, which of the following gives correct relationships for the values of  $\Delta G^{\circ}$  and  $K_{eq}$ ? [Electrochemistry, E]

 $\begin{array}{ll} (b) \ \Delta G^{\circ} > 0; \ K_{\rm eq} > 1 \\ (d) \ \Delta G^{\circ} < 0; \ K_{\rm eq} < 1 \end{array}$ (a)  $\Delta G^{\circ} > 0; K_{eq} < 1$ (c)  $\Delta G^{\circ} < 0; K_{eq} > 1$ 

- **12.** Which one of the following is incorrect for ideal solution? [Thermodynamics, M]
  - (a)  $\Delta H_{\rm mix} = 0$ (b)  $\Delta U_{\rm mix} = 0$ (c)  $\Delta P = P_{\text{observed}} - P_{\text{calculated by Raoult's law}} = 0$ (d)  $\Delta G_{\text{mix}} = 0$
- **13.** The solubility of AgCl(s) with solubility product  $1.6 \times 10^{-10}$  in 0.1 M NaCl solution would be

[Solutions, M]

(b)  $1.6 \times 10^{-9}$  M (a)  $1.26 \times 10^{-5}$  M (c)  $1.6 \times 10^{-11}$  M (d) zero

- **14.** Suppose the elements *X* and *Y* combine to form two compounds  $XY_2$  and  $X_3Y_2$ . When 0.1 mole of  $XY_2$ weighs 10 g and 0.05 mole of  $X_3Y_2$  weighs 9 g, the atomic weights of *X* and *Y* are
  - [Some Basic Concepts of Chemistry, M] (a) 40, 30 *(b)* 60, 40 (c) 20, 30 (d) 30, 20

- **15.** The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron =  $1.60 \times 10^{-19}$  C) [Electrochemistry, M]
  - (a)  $6 \times 10^{23}$  $(b)~6\times 10^{20}$ (c)  $3.75 \times 10^{20}$ (d)  $7.48 \times 10^{23}$
- **16.** Boric acid is an acid because its molecule (a) contains replaceable  $H^+$  ion
  - [Equilibrium, M] (b) gives up a proton
  - (c) accepts OH<sup>-</sup> from water releasing proton
  - (d) combines with proton from water molecule
- **17.** AlF<sub>3</sub> is soluble in HF only in the presence of KF. It is [Coordination Compounds, D] due to the formation of (a)  $K_3[AlF_3H_3]$ (b)  $K_3[AlF_6]$ (c)  $AlH_3$ (d) K[AlF<sub>3</sub>H]
- **18.** Zinc can be coated on iron to produce galvanised iron but the reverse is not possible. It is because (a) zinc is lighter than iron [Electrochemistry, M] (b) zinc has lower melting point than iron (c) zinc has lower negative electrode potential than iron (d) zinc has higher negative electrode potential than iron
- **19.** The suspension of slaked lime in water is known as [The s-block Elements-I, M]
  - (a) lime water
  - (b) quicklime
  - (c) milk of lime
  - (d) aqueous solution of slaked lime
- **20.** The hybridisations of atomic orbitals of nitrogen in  $NO_2^+$ ,  $NO_3^-$  and  $NH_4^+$ , respectively are (a) sp,  $sp^3$  and  $sp^2$ [Chemical Bonding, M]
  - (b)  $sp^2$ ,  $sp^3$  and sp

  - (c) sp,  $sp^2$  and  $sp^3$ (d)  $sp^2$ , sp and  $sp^3$
- **21.** Which of the following fluoro-compounds is most likely to behave as a Lewis base? [Equilibrium, M] (a)  $BF_3$ (b) PF<sub>3</sub> (c)  $CF_4$ (d)  $SiF_4$
- **22.** Which of the following pairs of ions is isoelectronic and isostructural? [Chemical Bonding, D]  $(a) \operatorname{CO}_{3}^{2-}, \operatorname{NO}_{3}^{-}$ (a)  $\operatorname{ClO}_3^-$ ,  $\operatorname{CO}_3^2$ (b)  $\operatorname{ClO}_3^-$ ,  $\operatorname{CO}_3^2$ (c)  $\operatorname{SO}_3^{2-}$ ,  $\operatorname{NO}_3^-$ (d)  $\operatorname{ClO}_3^-$ ,  $\operatorname{SO}_3^{2-}$
- **23.** In context with beryllium, which one of the following statements is incorrect? [The s-block Elements, D]
  - (a) It is rendered passive by nitric acid
  - (b) It forms  $Be_2C$
  - (c) Its salts rarely hydrolyse
  - (d) Its hydride is electron-deficient and polymeric

**EXAM SPECTRUM** 

24. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reaction does not show oxidising behaviour? [Redox Reactions, D]

$$\begin{array}{ll} (a) \operatorname{Cu} + 2\operatorname{H}_2 \operatorname{SO}_4 & \longrightarrow \operatorname{CuSO}_4 + \operatorname{SO}_2 + 2\operatorname{H}_2 \operatorname{O} \\ (b) & 3\operatorname{S} + 2\operatorname{H}_2 \operatorname{SO}_4 & \longrightarrow 3\operatorname{SO}_2 + 2\operatorname{H}_2 \operatorname{O} \\ (c) & \operatorname{C} + 2\operatorname{H}_2 \operatorname{SO}_4 & \longrightarrow \operatorname{CO}_2 + 2\operatorname{SO}_2 + 2\operatorname{H}_2 \operatorname{O} \\ (d) & \operatorname{CaF}_2 + \operatorname{H}_2 \operatorname{SO}_4 & \longrightarrow \operatorname{CaSO}_4 + 2\operatorname{HF} \end{array}$$

**25.** Which of the following pairs of *d*-orbitals will have electron density along the axes?

[Coordination Compounds, M]

- **26.** The correct geometry and hybridisation for XeF<sub>4</sub> are [Chemical Bonding, M]
  - (a) octahedral,  $sp^{3}d^{2}$
  - (b) trigonal bipyramidal,  $sp^{3}d$
  - (c) planar triangle,  $sp^{3}d^{3}$
  - (d) square planar,  $sp^{3}d^{2}$
- 27. Among the following, which one is a wrong statement? [The *p*-block Elements II, M]
  - (a)  $PH_5$  and  $BiCl_5$  do not exist
  - (b)  $p\pi$ - $d\pi$  bonds are present in SO  $_2$
  - (c)  $\,{\rm SeF}_4$  and  ${\rm CH}_4$  have same shape
  - (d)  $I_3^+$  has bent geometry
- 28. The correct increasing order of *trans*-effect of the following species is [Coordination Compounds, M]
  (a) NH<sub>3</sub> > CN<sup>-</sup> > Br<sup>-</sup> > C<sub>6</sub>H<sub>5</sub><sup>-</sup>

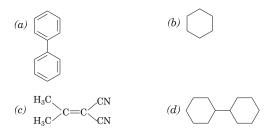
(b)  $\operatorname{CN}^- > \operatorname{C}_6\operatorname{H}_5^- > \operatorname{Br}^- > \operatorname{NH}_3$ 

- (c)  $Br^- > CN^- > NH_3 > C_6H_5^-$ (d)  $CN^- > Br^- > C_6H_5^- > NH_3$
- **29.** Which of the following statements related to lanthanons is incorrect? [The *d* and *f*-block Elements, M]
  - (a) Europium shows +2 oxidation state
  - $(b)\,$  The basicity decreases as the ionic radius decreases from  $\Pr$  to Lu
  - (c) All the lanthanons are much more reactive than aluminium
  - $(d)\ {\rm Ce}\ (+4)$  solutions are widely used as oxidising agent in volumetric analysis
- **30.** Jahn-Teller effect is not observed in high spin complexes of [Coordination Compounds, E] (a)  $d^7$  (b)  $d^8$ (c)  $d^4$  (d)  $d^9$
- **31.** Which of the following can be used as the halide component for Friedel-Crafts reaction?

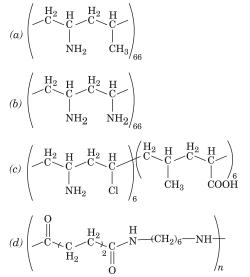
[Haloalkanes and Haloarenes, E]

- (a) Chlorobenzene
- (b) Bromobenzene
- (c) Chloroethene
- (d) Isopropyl chloride

**32.** In which of the following molecules, all atoms are coplanar? [Some Basic Principle and Techniques, M]



33. Which one of the following structures represents nylon-6 6 polymer? [Polymers, E]



**34.** In pyrrole



[Amines, E]

the electron density is maximum on(a) 2 and 3(b) 3 and 4(c) 2 and 4(d) 2 and 5

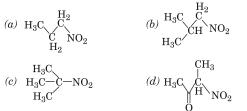
**35.** Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction? [Hydrocarbons, D]

(a) 
$$H_2C$$
— $CH_2$   
 $H_2$   
(b)  $H_3C$ — $C$ — $CH_2OH$   
(c)  $H_2C$ = $C$ = $O$   
 $H_2$   
(d)  $H_3C$ — $C$ — $CH_2Br$ 

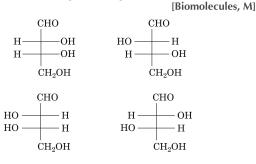
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**36.** Which one of the following nitro-compounds does not react with nitrous acid? [Amines, E]



- **37.** The central dogma of molecular genetics states that the genetic information flows from [Biomolecules, M]
  - (a) amino acids  $\rightarrow$  proteins  $\rightarrow$  DNA
  - (b)  $DNA \rightarrow carbohydrates \rightarrow proteins$
  - (c)  $DNA \rightarrow RNA \rightarrow proteins$
  - (d)  $DNA \rightarrow RNA \rightarrow carbohydrates$
- **38.** The correct corresponding order of names of four aldoses with configuration given below

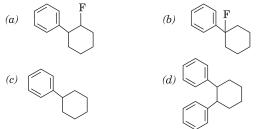


respectively, is

- (a) L-erythrose, L-threose, L-erythrose, D-threose
- (b) D-threose, D-erythrose, L-threose, L-erythrose
- (c) L-erythrose, L-threose, D-erythrose, D-threose
- (d) D-erythrose, D-threose, L-erythrose, L-threose

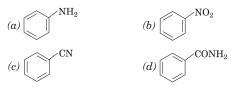
**39.** In the given reaction

the product P is [Some Basic Principles and Techniques, M]



**40.** A given nitrogen-containing aromatic compound A reacts with Sn/HCl, followed by  $\mathrm{HNO}_2$  to give an unstable compound B. B, on treatment with phenol, forms a beautiful coloured compound C with the

molecular formula C12H10 N2O. The structure of compound A is [Amines, D]



41. Consider the reaction, [Haloalkanes and Haloarenes, M] (

$$CH_{3}CH_{2}CH_{2}Br + NaCN \longrightarrow$$

 $CH_{3}CH_{2}CH_{2}CN + NaBr$ 

This reaction will be the fastest in

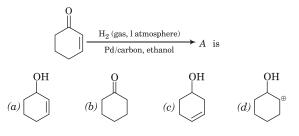
(a) ethanol

(b) methanol

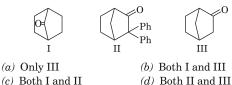
(c) N, N'-dimethylformamide (DMF)

(d) water

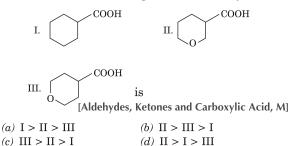
**42.** The correct structure of the product *A* formed in the reaction [Aldehydes, Ketones and Carboxylic Acids, M]



**43.** Which among the given molecules can exhibit tautomerism? [Some Basic Principles and Techniques, M]



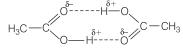
**44.** The correct order of strengths of the carboxylic acids

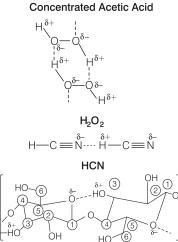


**45.** The compound that will react most readily with gaseous bromine has the formula [Hydrocarbons, M] (a)  $C_3H_6$ (b)  $C_2H_2$ (c)  $C_4 H_{10}$ (d)  $C_2H_4$ 

## **Answers** with **Explanation**

1. (c) Intermolecular hydrogen bonding present in concentrated acetic acid,  $H_2O_2$  and HCN while cellulose has intramolecular hydrogen bonding as shown below





#### Cellulose

In the above molecules, dotted lines represent hydrogen bonding.

**2.** (b) Key Idea The relation between molar conductivity  $(\lambda_m)$  and electrolytic conductivity  $(\kappa)$  is given as

$$\lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$

where, M is molarity of solution.

Given, concentration of solution,

 $M = 0.5 \text{ mol/dm}^3$ 

Electrolytic conductivity,

$$= 5.76 \times 10^{-3} \mathrm{S} \mathrm{cm}^{-1}$$

Temperature,  $T = 298 \,\mathrm{K}$ 

.:. Molar conductivity,

$$\lambda_{\rm m} = \frac{\kappa \times 1000}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5}$$
  
= 11, 52 S cm<sup>2</sup>/mol

**3.** (a)  $PH_3 \xrightarrow{W} P + \frac{3}{2}H_2$ 

This is an example of surface catalysed unimolecular decomposition.

For the above reaction, rate is given as

Rate = 
$$\frac{k\alpha p}{1 + \alpha p}$$

where, p = partial pressure of absorbing substrate. At low pressure,  $\alpha p \ll 1$ Rate =  $k \alpha p$ 

So,  $(\alpha p + 1)$  can be neglected.

Thus, the decomposition is predicted to be first order.

**4.** (c) Lower the coagulating power, higher is the coagulation value in millimoles per litre, i.e. coagulating power is inversely proportional to coagulation values. Thus, correct order of coagulating power is

 $MgSO_4 > BaCl_2 > NaCl \text{ or } III > II > I$ 

**5.** (b) Key Idea This problem is based on Faraday's first law of electrolysis which states that when an electric current is passed through an electrolytic solution, the amount of substance (w), deposited at the electrode, is proportional to the electric charge (q) passed through the electrolytic solution.

The formula used in the problem is

$$w = \frac{Eit}{96500} \qquad \dots (i)$$

where,  $E = \text{gram-equivalent mass of Cl}^$ i = current t = time it = a

Given, 
$$w = 0.10 \text{ mol} = (0 \cdot 10 \times 71) \text{ g},$$
  
 $i = 3 \text{ A}, E = 35.5$ 

The following reactions occur at electrodes

At cathode 
$$2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$$

At anode 
$$2\operatorname{Cl}^- \xrightarrow{-2e^-} \operatorname{Cl}_2$$
  
35.5g  $\xrightarrow{71 \text{ g}}$ 

or

*:*..

Putting all the values in expression (i) we get  

$$(0.10 \times 71) = \frac{35.5}{20522} \times 3 \times t$$
 or  $t = 6433$  s

$$96500$$
  
 $t = 107 22 min$ 

 $\int 1s = \frac{1}{60} \min \int$ 

**6.** (*a*) According to Hund's rule of maximum multiplicity, An orbital can accommodate a maximum number of 2 electrons of exactly opposite spins. Hence, option (*a*) is correct.

**Caution** Remember, maximum number of electrons in an orbital do not depend upon the quantum numbers as given in the question.

7. (b) Entropy change is given as,

$$\Delta S = n C_p \ln \frac{T_f}{T_i} + n R \ln \frac{p_i}{p_f} \qquad \dots (i)$$

For isothermal process,  $T_i = T_f$ 

$$nC_p \ln \frac{T_f}{T_i} = nC_p \ln \frac{T_i}{T_i} = 0 \qquad [\ln 1 = 0]$$

From Eq. (i) 
$$\Delta S = nR \ln \frac{p_i}{p_f}$$

 (d) Key Idea Strong electrolytes dissociate completely in their solutions. van't Hoff factor = total number of ions after dissociation

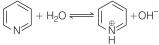
So, for Ba(OH)<sub>2</sub>  $\implies$  Ba<sup>2+</sup>(*aq*) + 2OH<sup>-</sup>(*aq*)

Number of ions 1 2 van't Hoff factor, i = 1 + 2 = 3

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**9.** (b) The percentage of pyridine can be equal to the percentage of dissociation of pyridinium ion and pyridine solution as shown below:

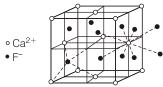


As pyridinium is a weak base, so degree of dissociation is given as

$$\begin{aligned} \alpha &= \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7 \times 10^{-9}}{0.10}} \\ &= \sqrt{1.7 \times 10^{-8}} = 1.3 \times 10^{-4} \end{aligned}$$

or percentage of dissociation =  $(\alpha \times 100)\%$ =  $(1.3 \times 10^{-4}) \times 100 = 0.013\%$ 

- $=(1.3 \times 10^{-4}) \times 100 = 0.013\%$
- **10.** (c)  $\ln \operatorname{CaF}_2$  (Fluorite structure),  $\operatorname{Ca}^{2+}$  ions are arranged in ccp arrangement ( $\operatorname{Ca}^{2+}$  ions are present at all corners and at the centre of each face of the cube) while  $F^-$  ions occupy all the tetrahedral sites.



From the above figure, you can clearly see that coordination number of  $F^-$  is 4 while that of  $Ca^{2+}$  is 8.

**11.** (a) Given, 
$$E_{\text{cell}}^{\circ} = -\text{ve}$$

Now, the relation between  $\Delta G^{\circ}$  and  $E_{cell}^{\circ}$  is given as

$$\Delta G^{\circ} = -nF \ E_{\text{cell}}^{\circ} \qquad \dots (i)$$

as  $E_{cell}^{\circ}$  is negative , so  $\Delta G^{\circ}$  comes out to be positive. Again, relation between  $\Delta G^{\circ}$  and  $K_{eq}$  is given as

$$\Delta G^{\circ} = -2.303nRT \log K_{eq} \qquad \dots (ii)$$

 $\begin{array}{ll} \mbox{From Eq. (i) we get that } \Delta G^\circ \mbox{ is positive. Now, if } \Delta G^\circ \mbox{ is positive then } K_{\rm eq} \mbox{ comes out to be negative from eq (ii).} \\ \mbox{i.e.} \qquad \Delta G^\circ > 1 \mbox{ and } K_{\rm eq} < 1 \end{array}$ 

**Short Trick** As  $E_{cell}^{\circ}$  is negative so reaction is non-spontaneous or you can say reaction is moving in backward direction.

For non-spontaneous reaction,  $\Delta G^\circ$  is always positive and  $K_{\rm eq}$  is always less than 1.

**12.** (*d*) Key Idea For this problem, the following expression can be used.

$$\Delta G_{\rm mix} = \Delta H_{\rm mix} - T \Delta S_{\rm mix}$$

For an ideal gas

....

 $\Delta H_{\rm mix}$  = 0;  $\Delta U_{\rm mix}$  = 0;  $\Delta S_{\rm mix}$  ≠ 0 Putting all these values in the expression,

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$
$$\Delta G_{\text{mix}} = 0 - T\Delta S_{\text{mix}}$$
$$\Delta G_{\text{mix}} \neq 0$$

Thus, option (d) is incorrect.

 (b) Key Idea As solubility of AgCl(s) is asked in 0.1 M NaCl, so in the calculation, solubility of CI<sup>-</sup> (from NaCl) must be added to the solubility of CI<sup>-</sup> (from AgCl).

Let s be the solubility of Ag  $^+{\rm and}$  Cl  $^-$  in AgCl before the addition of NaCl.

NaCl(aq) → Na<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)  
0.1 M 0 0  
0 0.1 M 0.1+s  
AgCl(s) → Ag<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)  
s s+0.1  
Given, 
$$K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$$
  
or  $1.6 \times 10^{-10} = s(0.1 + s)$   
 $= 0.1 s + s^2$   
∵  $K_{sp}$  is small, so s is very less in comparison

 $\begin{array}{ll} \because K_{\rm sp} \text{ is small, so } s \text{ is very less in comparison with 0.1.} \\ \text{Hence, } s^2 \text{ can be neglected.} \\ \text{Thus, } 1.6 \times 10^{-10} = 0.1 \, s \\ \text{or} \qquad \qquad s = 1.6 \times 10^{-9} \, \text{M} \end{array}$ 

**14.** (a) Let, atomic masses of X and Y be  $A_X$  and  $A_Y$ , respectively

For 
$$XY_2$$
,  $n_{XY_2} = 0.1 = \frac{10}{A_X + 2A_Y}$   
or  $A_X + 2A_Y = 100$  ...(i)  
For  $XY_2$   $n_X = 0.05 = -\frac{9}{2}$ 

For  $X_3Y_2$ ,  $n_{X_3Y_2} = 0.05 = \frac{1}{3A_X + 2A_Y}$ or  $3A_X + 2A_Y = 180$ 

On solving Eqs. (i) and (ii), we get

$$A_X = 40 \text{ g mol}^{-1}$$
  
 $A_Y = 30 \text{ g mol}^{-1}$ 

**15**. (c) From Faraday's first law of electrolysis,

$$\frac{w}{E} = \frac{it}{96500} \qquad \dots (i)$$

...(ii)

Given, i = 1 A; t = 60 s

Putting these values in Eq. (i), we get

$$\frac{w}{E} = \frac{1 \times 60}{96500}$$

or  $\frac{w}{E} = \frac{6}{9650}$ 

= Number of mole of electrons

:. Number of electrons = 
$$\frac{6}{9650} \times 6.022 \times 10^{23}$$
  
=  $3.75 \times 10^{20}$ 

**16.** (c) Boric acid can be considered as an acid because its molecule accepts OH<sup>-</sup> from water, releasing proton.

$$\begin{array}{ccc} H_{3}BO_{3} + H_{2}O \Longrightarrow B(OH)_{4}^{-} + & H^{+} \\ Acid & Base & Conjugate \\ base & base & acid \end{array}$$

**Remember** In the given options to the question, (a), (b) and (c) are correct as all of these sentences have more or less similar meaning but here (c) option is the most appropriate one as it gives complete explanation of the fact that how boric acid can be combined with an acid.

#### 🔁 EXAM SPECTRUM

**17.** (b) Key Idea  $AI^{3+}$  shows maximum coordination number 6, thus it will form  $AIF_6^{3-}$ .  $AIF_3$  forms  $K_3[AIF_6]$  when dissolved in HF in the presence of KF as shown below:

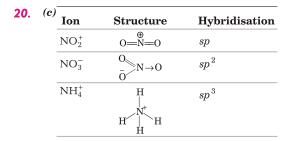
$$AlF_3 + 3KF \xrightarrow{HF} K_3[AlF_6]$$

**18.** *(d)* The metal with higher negative standard reduction potential, have higher tendency to get reduced.

$$\operatorname{Zn}^{2+} + 2e^{-} \longrightarrow \operatorname{Zn}; \quad E^{\circ} = -0.76 \,\mathrm{V}$$
  
$$\operatorname{Fe}^{2+} + 2e^{-} \longrightarrow \operatorname{Fe}; \quad E^{\circ} = -0.44 \,\mathrm{V}$$

Here, in galvanised iron, Zn has higher negative reduction potential means Zn takes electrons given by iron and itself gets reduced. Thus, Zn works as anode and protects iron from rusting by making iron as cathode.

**19.** (c) Aqueous solution of slaked lime is called lime water whereas suspension solution of slaked lime is called milk of lime.

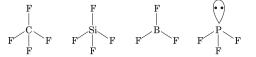


Thus, option (c) is correct.

**Time saver** You can catch the option very easily if you know NO $_2^+$  has sp and NH $_4^+$  has sp<sup>3</sup>-hybridisation.

**21.** (b) Key Idea The molecule with lone pair at centre atom, will behave as Lewis base.

In the given molecules, only  $\mathrm{PF}_3$  has lone pair at P as shown below:



Thus,  $\mbox{PF}_3$  acts as a Lewis base (electron-pair donor) due to the presence of lone pair on P-atom.

#### **22.** (a, d)

Species	Total number of electrons	Structure	Shape
$ClO_3^-$	42		Pyramidal
$SO_3^{2-}$	42		Pyramidal
$\overline{\mathrm{CO}_3^{2-}}$	32		Trigonal planar
$NO_{\overline{3}}$	32		Trigonal planar

Hence, both options (a) and (d) are correct.

23. (c) Beryllium salts are covalent in nature because of very small Be<sup>2+</sup> ion and its high polarising power, it is easily hydrolysed.

 $\operatorname{BeCl}_2 + 2\operatorname{H}_2\operatorname{O} \longrightarrow \operatorname{Be(OH)}_2 + 2\operatorname{HCl}$ 

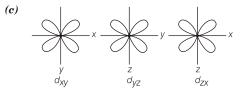
24. (d) Key Idea An oxidising agent is a species, which oxidises the other species and itself gets reduced.

(i) 
$$C \stackrel{0}{u} + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$
  
(ii)  $3\stackrel{0}{S} + 2H_2SO_4 \longrightarrow 3\stackrel{+4}{SO}_2 + 2H_2O$   
(iii)  $\stackrel{0}{C} + H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$   
(iv)  $\stackrel{+2}{Ca}\stackrel{-1}{F}_2 + H_2SO_4 \longrightarrow \stackrel{+2}{Ca}SO_4 + 2H\stackrel{-1}{F}$ 

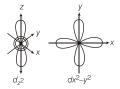
e.g.

25.

In reaction (iv), oxidation number of elements remains unchanged. Thus, in this reaction,  $\rm H_2SO_4$  does not act as an oxidising agent.



Thus,  $d_{xy}, d_{yz}$  and  $d_{zx}$  orbitals have maximum electron density between the axes.



 $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals have maximum electron density along the axes.

**26.** (*d*) **Key Idea** Hybridisation is determined by electron pair arrangement whereas geometry is determined by arrangement of atoms around the centre atom.



Geometry : square planar, Hybridisation  $-sp^{3}d^{2}$ Thus, option (d) is correct.

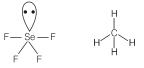
**27.** (c)  $PH_5$  does not exist due to very less electronegativity difference between P and H. Hydrogen is slightly more electronegative than phosphorus, thus could not hold significantly the sharing electrons.

On the other hand,  ${\rm BiCl}_5$  does not exist due to inert pair effect.

On moving down the group, +5 oxidation state becomes less stable while +3 oxidation state becomes more stable.

In SO  $_2$ ,  $p\pi$ - $d\pi$  and  $p\pi$ - $p\pi$  both types of bonds are present

#### **EXAM SPECTRUM**





Thus,  $SeF_4$  and  $CH_4$  do not have same shape.



Geometry-Bent

Thus, option (c) is incorrect statement.

**28.** (b) *Trans*-effect is the effect of a coordinated group upon the rate of substitution at the position *trans* to itself in a square or octahedral complex. As the rate of substitution of the *trans* ligand increases, the intensity of *trans* effect also increases. Thus, correct order is,

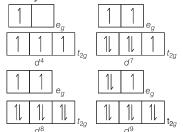
$$CN^- > C_6H_5^- > Br^- > NH_3$$

(c) 
$$\operatorname{Eu}(63) = 4f^7 \cdot 5d^0, 6s^2, \operatorname{Eu}^{2+} = 4f^7$$

29.

In lanthanoids series, ionic radius decreases and covalent character increases, thus basicity decreases. Lanthanons are less reactive than aluminium due to high ionisation potential. The reason for this high ionisation potential is lanthanoid contraction.

- ${\rm Ce}^{4+}$  is a good oxidising agent, it is easily converted to  ${\rm Ce}^{3+}.$
- (b) Key Idea Jahn-Teller distortion is observed in those octahedral complexes in which d-electrons are filled unsymmetrically.



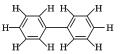
Except  $d^8$ , all are unsymmetrically filled, thus  $d^8$  complex will not show Jahn-Teller distortion.

(d) Key Idea In chlorobenzene, bromobenzene and chloroethene, lone pair of halogen is delocalised with π-bonds so C—X attains double bond character. Thus, these are not suitable as a halide component for Friedel-Crafts reaction.

Other halides, i.e. chloro and bromobenzene along with chloroethene have carbon halogen bond as

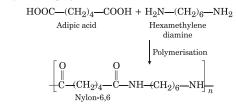


**32.** (a) The molecule in which all the carbon atoms are  $sp^2$ -hybridised will be coplanar. Thus, in option (a) i.e.



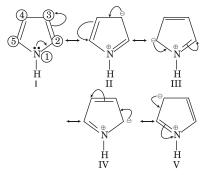
all carbons are *sp*<sup>2</sup>-hybridised.

**33.** (*d*) Nylon-6 6 polymer is formed as



Thus, option (d) is correct.

**34.** *(d)* The conjugation (delocalisation) of electrons in pyrrole can be visualised as



As resonating structures III and IV are more stable than II and V. Thus, maximum electron density will be found on carbon 2 and 5.

**35**. (c) The said reactions can be visualised as

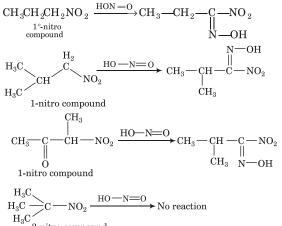
$$\begin{array}{c} H_{2}C \longrightarrow CH_{2} & \xrightarrow{HBr} CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} & \xrightarrow{Br} \\ & \downarrow \\ & Electrophilic \\ & addition \end{array} CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} & \xrightarrow{CH_{2}} CH_{2} & \xrightarrow{CH_{2}} CH_{2} \\ CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow OH & \xrightarrow{HBr} \\ CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow Br & \xrightarrow{Br} \\ CH_{2} = C = O \xrightarrow{HBr} \\ CH_{2} = C = O \xrightarrow{HBr} \\ CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow Br \\ \xrightarrow{CH_{3}} CH_{2} \longrightarrow CH_{2} \longrightarrow Br \\ CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{2} \longrightarrow CH$$

Thus, option (c) is correct.

**EXAM SPECTRUM** 

**36.** (c) Key Idea 1° and 2° nitro compounds react with HNO<sub>2</sub> while 3°-nitro compound does not.

The reactions of connected compounds are



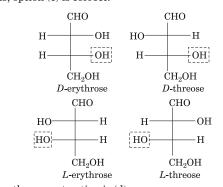
3-nitro compound

Thus, option (c) is incorrect.

**37.** (c) The central dogma of molecular genetics states that  $DNA \xrightarrow{\text{Transcription}} RNA \xrightarrow{\text{Translation}} Protein$ 

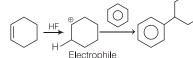
 $DNA \longrightarrow RNA \longrightarrow Protei$ Thus, option (c) is correct.

**38**. (d)



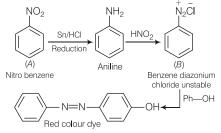
Thus, the correct option is (d).

**39.** (c) Key Idea It is an example of Friedel-Craft reaction. First  $\pi$ -electrons of cyclohexene attack at H<sup>+</sup> ion of HF and form carbocation. This carbocation further reacts with benzene and forms addition product.



Thus, the correct option is (c).

**40**. (b) The complete road map of the reaction can be seen as



**41.** (c) The given reaction follows  $S_N 2$  mechanism and  $S_N 2$  reactions are favoured in polar aprotic medium like DMSO, DMF... etc.

 $CH_{3}CH_{2}CH_{2}Br + NaCN \xrightarrow{DMF} CH_{3}CH_{2}CH_{2}CN + NaBr$ 

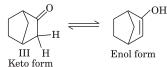
So, the correct option is (c).

**42.** (b) In the presence of Pd-catalyst, selective reduction of  $\alpha,\beta$ -unsaturated carbonyl is observed as hydrogenation takes place of carbon-carbon double bond only.



(a) In tautomerism, α-hydrogen must be present in the molecule. Thus, molecule II will not show tautomerism. As at bridge, double bond is highly unstable. So, molecule I will also not show tautomerism.

For III molecule,

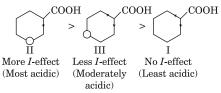


So only, molecule III will show tautomerism. Thus, correct option is (*a*).

**44.** (b) Key Idea Order of strengths of the given carboxylic acids can be determined by the concept of -I-effect.

The oxygen atom present in the ring shows -*I*-effect. As the distance between oxygen and —COOH group increases, -*I*-effect of oxygen decreases.

Thus, corresponding carboxylic acid will show less acidic nature. The correct order of strengths of the carboxylic acids is



**45.** (a) In gaseous state,  $Br_2$  forms free radicals. Br attacks at allylic hydrogen of propene and forms stable allylic free radical. Thus, propene (C<sub>3</sub>H<sub>6</sub>) will react most readily with gaseous bromine and gives allylic substitution reaction.

Allylic free radical is more stable due to the delocalisation of unpaired electron over two carbon atom.

 $\dot{C}H_2 \xrightarrow{\checkmark} CH = CH_2 \longleftrightarrow CH_2 = CH - \dot{C}H_2$ 



# Elements How They were Discovered Part 4 **TIN AND LEAD**

In July 2016 issue, we have read about copper and iron. Now, we are going to read discoveries and properties of lead and tin in this issue. Lead and tin are commonly used for protective coating of materials susceptible to weathering. Now-a-days, tin is used in cans for foods and lead is used in lead-acid storage batteries.

#### Tin

- Tin also has been known since, ancient times. It is believed that it was discovered about 6 to 6.5 thousand years ago, i.e. in the same period as that of copper.
- The latin name for tin (stannum), stems from the Sanskrit stan which means 'solid'. The chemical symbol Sn orginates from latin name.
- In the bronze age period, tin was used in bronze alloy. Bronze alloy contains roughly 90% of copper and 10% of tin. The peoples of Egypt, Mesopotamia and the Indus Valley started using tin around 3 thousand years ago.
- Tin was widely known in the countries of the Mediterranean sea region, Persia and India.
- The Ancient Greeks obtained tin by sea-trade and referred to the source as "The Cassiterides" meaning tin islands.
- The oldest known tin articles were found in burial sites of the 18th dynasty (1580-1350 B.C.) in particular a ring or a vessel.
- Tin was also found in America when Cortez arrived in South America in 1519, he found that tin coins were widely circulating in Mexico. However, the time of discovery is not known.
- Besides using as a component of bronze, tin was also used for making crockery and jewellery. Pliny the Elder and Dioskorides mention tinning of copper plates to protect them from corrosion.
- Upto 13th century, England was the only country in Europe where tin was produced. In mid 16th century the cost of tin was equal to that of silver and it was used for manufacturing luxury goods. As its production increased it was used in many other things, for instance, for making tin plate.
- Today, the world's largest producer of tin is China followed by Indonesia. At the moment world demand for tin exceeds its production. Global demand is presently at about 366000 tons, worth approximately 700 crore, with production about 6000 tons short.

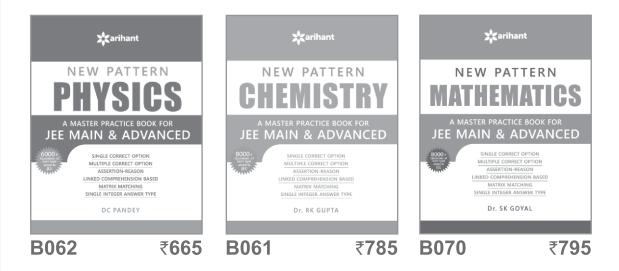
#### Lead

- Lead has been known since, ancient times. No one is quite sure how lead got its name. It became known to Egyptians simultaneously with iron and silver.
- It is rarely occurred in a native state but is smelted fairly easily from its ores.
- Lead was been mined for more than 6000 yrs and was produced as early as 2000 B.C. in India and China. However, in Europe production of lead began in 600 B.C.
- Lead was confused with tin for a long time because of their names on that time. Tin was named as "plumbum album" and lead—"plumbum nigrum". In the middle ages, they were recognised as different metals.
- Greeks and Phoenicians started many lead mines in Spain which later were taken over by Romans.
- Romans widely used the metal lead in ancient times. They used lead for making crockery, pipes and writing tablets. Lead was also used for manufacturing white lead. The Island of Rhodes was the biggest exporter of white lead.
- White lead is prepared by immersing lead pipes into vinegar, the salt thus obtained is boiled with water for a long time.
- Red lead was first obtained unexpectedly. When a fire broke out in the Greek port of Piraeus barrels with lead were enveloped in flames. After the fire had been extinguished, red substance was found in the charred barrels it was red lead.
- Today Scientists believe that many Romans might become ill and died because of using lead in daily practice when food was cooked, in lead utensils, lead was dissolved into the food. People who ate this food got more and more lead into their bodies. As lead is toxic, teratogenic and carcinogenic, it causes serious health problems.
- After the invention of firearms lead, it was used for making bullets.
- Lead has many peaceful applications also, e.g. typographical types are made of its alloy with antimony. Lead was also used for protection against radiation in experiments.

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- SINGLE INTEGER ANSWER TYPE, etc.





# JEE ADVANCED DRILL

A collection of 30 innovative problems on JEE Advanced pattern from complete syllabus

#### **Single Answer Correct Type**

- **7.** An element crystallises as face-centred cubic lattice. Its density is 8.20 g cm<sup>-3</sup> and the length of side of the unit cell is 3.66 Å. The number of atoms present in 200 g of the element is  $(a) 1 \times 10^{24} \quad (b) 2 \times 10^{24} \quad (c) 3 \times 10^{24} \quad (d) 4 \times 10^{24}$
- **2.**  $PbCl_4$  exists, but  $PbBr_4$  and  $PbI_4$  do not exist because
  - (a) strong reducing character of  $Pb^{4+}$
  - (b) strong oxidising character of Pb<sup>4+</sup>
  - (c) large size of  $\rm Br^-$  and  $\rm I^-$
  - (d) low electronegativity of bromine and iodine
- **3.** Which of the following statements are correct regarding  $[Cu(NH_3)_4]^{2+}$  ion?
  - I. It involves *sp*<sup>3</sup>-hybridisation with tetrahedral geometry.
  - II. Cu is tetracoordinated and exists as square planar complex.
  - III. It involves  $dsp^2$ -hybridisation.
  - IV. It involves  $sp^2d$ -hybridisation.

Select the correct option.

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

- 4. The major product of debromination with KI in acetone solution of erythro or meso-2, 3-dibromobutane is

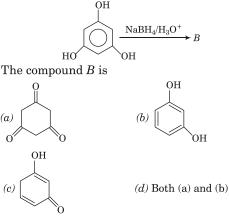
  (a) butene
  (b) n-butane
  (c) trans-but-2-ene
  (d) cis-but- 2-ene
- 5. The specific rotation of  $\alpha$ -glucose is +112° and  $\beta$ -glucose is + 19° and the specific rotation of the constant equilibrium mixture is + 52.7°. The percentage composition mixture of anomers ( $\alpha$  and  $\beta$ ) in the equilibrium mixture is

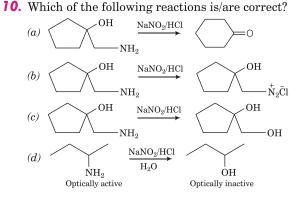
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(a) 46.3%, 63.8%
```

- (b) 36.2%, 68.3%
- (c) 36.2%, 63.8%
- $(d) \ 32.6\%, \ 68.3\%$

#### One or More than One Answer Correct Type

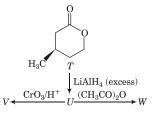
- **6.** Which of the following are the examples of heterogeneous catalytic reactions?
  - (a) Hydrogenation of vegetable oils
    - Vegetable oil +  $H_2 \xrightarrow{Ni}$  Vegetable ghee
  - (b) Synthesis of methanol,
    - $CO + 2H_2 \xrightarrow{Cu, ZnO Cr_2O_3} CH_3OH$
  - (c) Haber's process reaction
  - (d) Ostwald's process reaction
- 7. Which of the following statements is/are correct?
  - (a) Pure alumina does not electrolyse
  - (b) Calcination of ore of copper is done in its extraction from chalcocite
  - (c) Carbon can reduce CuO but does not reduce CaO
  - $(d)\,{\rm ZnO}\,{\rm is}\,{\rm used}\,{\rm to}\,{\rm remove}\,{\rm impurity}\,{\rm of}\,{\rm CaO}\,{\rm present}\,{\rm in}\,{\rm an}\,{\rm ore}$
- 8. Which of the following statements is/are not true?
  (a) Hg<sup>+</sup> is paramagnetic, while Hg<sup>2+</sup> is diamagnetic
  (b) Among U<sup>3+</sup>, Cm<sup>4+</sup> and Th<sup>4+</sup>, Th<sup>4+</sup> ion is colourless
  (c) Zinc shows variable valency
  (d) La(OH)<sub>3</sub> is more basic than Lu(OH)<sub>3</sub>
- **9.** Phenols are generally not changed with  $NaBH_4/H_3O^+$ . However, 1, 3, 5,-benzenetriol gives a high yield of product(*B*),





**11.** Which of the following statements is/are correct?

- (a) Nylon-6 6 is the polymer of adipic acid and sebasic acid (b) Phenol formaldehyde resin (Resol or Novolac) is
- formed when the phenol/formaldehyde (P/F) ratio is greater than 1
- (c) Terylene or dacron is a condensation polymer
- (d) Natural rubber is *cis*-rubber, while synthetic rubber is trans rubber
- 12. With reference to the scheme given, which of the given statements about T, U, V and W is/are correct? [IIT JEE 2012]



- (a) T is soluble in hot aq. NaOH
- (b) U is optically active
- (c) Molecular formula of W is  $C_{10}H_{18}O_4$

**13.** Reduction of metal centre in aqueous permanganate ion involves (a) three electrons in neutral medium (b) five electrons in neutral medium

- (c) three electrons in alkaline medium
- (d) five electrons in acidic medium

#### Integer Type

**14.** In the chemical reaction,

$$HOCH_2 \longrightarrow C \longrightarrow (CHOH)_3 \longrightarrow CH_2OH \longrightarrow CH_2OH$$

The number of formed HCOOH molecule(s) is

**15.** The reversible reduction potential of pure water in -0.414 V under 1.00 atm H<sub>2</sub> pressure. If the reduction is considered to be

$$2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H}_2.$$

The hydrogen ion concentration of pure water in the multiple of  $10^{-7}$  is

- **16.** The initial concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 30 s. How much time (in sec) will be taken in 20% completion of the reaction?
- **17.** Depression in freezing point of 0.01 mole of aqueous solution of propanoic acid is 0.02046°C. 0.1 molal glucose solution freezes at – 0.186°C. Assuming molality of solution is equal to its molarity, pH of propanoic acid solution would be nearly.
- **18.** Among the complexes,  $[Cr(NH_3)_6] [Co(CN)_6], [Co(py)_2(H_2O)_3Cl]Cl_2,$  $[Pt(NH_3)_4Br_2] Cl_2, [Co(NH_3)_5(NO_2)] Cl_2$ and  $[Cu(NH_3)_4]$  [PtCl<sub>6</sub>], the number of complexes that show coordination isomerism is

**19.** 
$$R \longrightarrow C \longrightarrow R \longrightarrow R \longrightarrow CH_2 \longrightarrow R$$

 $\cap$ 

Identify the numbers of reagent that can be used for the above conversion.

(i) 
$$\operatorname{Zn-Hg}/\operatorname{HCl}$$
 (ii)  $\operatorname{LiAlH}_4$ 

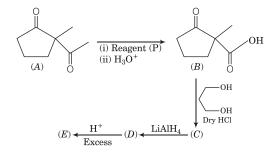
(iii) 
$$CHCl_3 + NaOH$$
 (iv)  $N_2H_4/OH$   
(v)  $\begin{vmatrix} CH_2 - SH \\ CH_2 - SH \end{vmatrix}$ ,  $H_2/Ni$ 

- **20.** In dil.  $H_2SO_4$ , aq.the complex diaquadioxalatoferrate(II) is oxidised by MnO<sub>4</sub>. For this reaction, the ratio of the rate of change of  $[H^+]$  to the rate of change of  $[MnO_4^-]$  is [IIT JEE 2015]
- **21**. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is  $2.0 \mathrm{g} \mathrm{cm}^{-3}$ . The ratio of the molecular weights of the

solute and solvent, is [IIT JEE 2016]  $m_{
m solvent}$ 

#### **Comprehension 1**

Consider the following reaction flow :



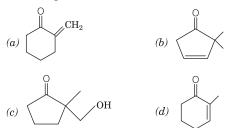
- **22.** The reagent P is
  - $(b) \operatorname{Br}_2 / \overline{\operatorname{O}} \operatorname{H}$ (a) NaOI (d) All of these  $(c) \operatorname{Ca(OH)}_2 + \mathrm{I}_2$

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- [IIT JEE 2011]

- (d) V gives effervescence on treatment with aq. NaHCO<sub>3</sub>

#### **23.** The compound E is



#### **Comprehension 2**

Thermal decomposition of gaseous  $X_2$  to gaseous X at 298 K takes place according to the following equation,

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard Gibbs free energy,  $\Delta_r G^\circ$ , of this reaction is positive. At the start of the reaction, there is one mole of  $X_2$ and no X. As the reaction proceeds, the number of moles of X formed is given by  $\beta$ . Thus,  $\beta_{\text{equil.}}$  is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given, R = 0.083 L bar  $\text{K}^{-1} \text{ mol}^{-1}$ ) [IIT 2016]

**24.** The equilibrium constant,  $K_p$  for this reaction at

298 K, in terms of  $\beta_{equil.}$  is

$$\begin{array}{l} (a) \ \displaystyle \frac{8 \ \beta_{equil.}^2}{2 - \beta_{equil.}} \\ (b) \ \displaystyle \frac{4 \ \beta^2 \ equil.}{4 - \beta^2 \ equil.} \\ (c) \ \displaystyle \frac{4 \ \beta^2 \ equil.}{2 - \beta_{equil.}} \\ \end{array} \end{array}$$

- **25.** The incorrect statement among the following for this reaction, is
  - (a) decrease in the total pressure will result in the formation of more moles of gaseous  ${\cal X}$
  - (b) at the start of the reaction, dissociation of gaseous  $X_{\rm 2}$  takes place spontaneously
  - (c)  $\beta_{\text{equil.}} = 0.7$

$$(d) K_C < 1$$

#### **Comprehension 3**

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (-57.0 kJ mol<sup>-1</sup>), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

[IIT JEE 2015]

26. Enthalpy of dissociation (in kJ mol<sup>-1</sup>) of acetic acid obtained from the Expt. 2 is

(a) 1.0  (b) 10.0  (c) 24.5  (d) = 0	51.4
--------------------------------------	------

**27.** The pH of the solution after Expt. 2 is (a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

#### Matrix Type

28

**[IIT IEE 2016]** 

<b>Column I</b> (Carbohydrates)	<b>Column II</b> (Characteristics)
A. D-glucose	p. Non-reducing
B. D-fructose	q. Osazone
C. Lactose	r. Reducing
D. Sucrose	s. Polysaccharide
E. Starch	

А	В	С	D	Е
(a) r,r	r,s	p,q	q	$^{\rm s,q}$
(b) q,r	q,r	q,r	р	$_{\rm p,s}$
(c) p	$^{\rm s,q}$	р	$\mathbf{r}$	$_{\rm p,s}$
(d) s,r	$\mathbf{q}$	p,q	$\mathbf{s}$	p,r

**29.** Match the anionic species given in Column I that are present in the ore(s) given in Column II. [IIT JEE 2015]

Column I				Column II	
A. Carbonate				p. Siderite	
В. 5	Sulphi	de		q. Malachite	
C. Hydroxide				r. Bauxite	
D. Oxide			s. Calamine		
				t. Argentite	
Codes					
А	В	С	D	A B C D	
(a) q,s	s,t	$\mathbf{r}$	р	(b) p,q,s t q,r r	
(c) q,r	p,s	t	r	(d) p,s q,t s r	

**30.** All the compounds listed in Column I react with water. Match the result of the respective reaction with the appropriate options listed in Column II. [IIT JEE 2010]

Column I				Column II
A. $(CH_3)_2SiCl_2$			p.	Hydrogen halide formation
B. $XeF_4$			q.	Redox reaction
C. $Cl_2$			r.	Reacts with glass
D. $VCl_5$			s.	Polymerisation
			t.	$O_2$ formation
Codes				
Α	В	С	D	
(a) p,s	s,t	r,s	$\mathbf{q}$	
(b) p,s	p,q,r,t	p,q,t	$\mathbf{s}$	
(c) p	r,s	t	$\mathbf{s}$	
(d) q	$^{\rm s,t}$	p,q	r	

## **Answers** with **Explanation**

#### **1**. (b) Given that,

•:•

Density (
$$\rho$$
) = 8.20 g cm<sup>-3</sup>  
 $Z = 4$  (fcc lattice)  
 $a = 3.66$  Å  
 $N_A = 6.023 \times 10^{23}$   
 $\rho = \frac{Z \times M}{a^3 \times N_A}$   
8 20 =  $\frac{4 \times M}{a^3 \times M_A}$ 

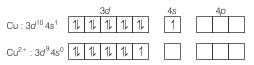
$$8.20 = \frac{4 \times 10^{-8}}{(3.66 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

or M = 60.54

... Number of atoms in 200 g of element

$$=\frac{200}{60.54}\times 6.023\times 10^{23}=1.99\times 10^{24}\approx 2\times 10^{24}$$

- **2.** (b) Due to strong oxidising character of Pb<sup>4+</sup>, it oxidises  $Br^-$  and  $I^-$  to  $Br_2$  and  $I_2$  respectively which by themselves are reducing in nature. This reaction is not given by Cl<sup>-</sup>.
- **3.** (b) Physical measurements have indicated that tetrahedral geometry for  $[Cu(NH_3)_4]^{2+}$  is not possible.

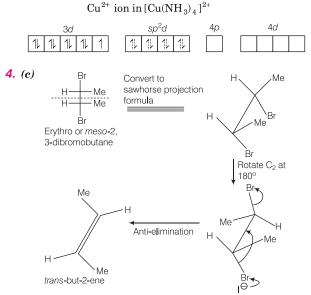


For dsp ^-hybridisation 3d-electron must be excited to 4p as follows :



In the above configuration, the unpaired electron present in 4p-orbital which is higher in energy and should be expected to be easily lost and Cu<sup>2+</sup> oxidised to Cu<sup>3+</sup> but it never occur.

Huggins suggested  $sp\,^2d\mathchar`-$  hybridisation for  $[{\rm Cu}({\rm NH}_3)_4\,]^{2+}$  ion



 (c) Let, at equilibrium, percentages of α and β-glucose are a and b% respectively.

Equilibrium specific rotation

 $(a \times \text{specific rotation of } \alpha \text{-glucose})$ 

$$= \frac{+(b \times \text{specific rotation of } \beta - \text{glucose})}{100}$$
  

$$\Rightarrow + 52.7 = \frac{a \times 112 + b \times 19}{100}$$
  

$$\Rightarrow + 52.7 = \frac{112 a + (100 - a) \times 19}{100} = \frac{112a + 1900 - 19a}{100}$$
  

$$\Rightarrow 5270 = 112a + 1900 - 19a$$

Solving for *a* and *b*, a = 36.2%, b = 63.8%.

**6.** (*a*, *b*, *c*, *d*) Key Concept When the catalyst is in different phase than the reactants, it is called heterogeneous catalyst and this type of process is called heterogeneous catalysis. In heterogeneous catalysis, the catalyst is generally a solid and the reactants are generally gases, but sometimes liquid reactants are also used.

All the reactions mentioned in the options, are the examples of heterogeneous catalytic reactions.

Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst,

Vegetable  $\operatorname{oil}(l) + \operatorname{H}_2(g) \xrightarrow{\operatorname{Ni}(s)} \to \operatorname{Vegetable}$  ghee (s) Synthesis of methanol

$$\operatorname{CO}(g) + 2\operatorname{H}_2(g) \xrightarrow{\operatorname{Cu}, \operatorname{ZnO}, \operatorname{Cr}_2\operatorname{O}_3} \operatorname{CH}_2\operatorname{OH}(l)$$

In the Haber's process,

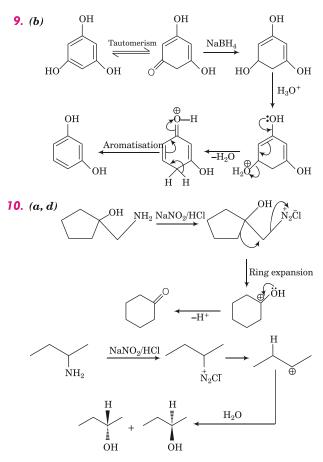
$$\operatorname{N}_2(g) + \operatorname{3H}_2(g) \xrightarrow{\operatorname{Fe}(s)} \operatorname{2NH}_3(g)$$

In Ostwald's process,

$$4\mathrm{NH}_3(g) + 5\mathrm{O}_2(g) \xrightarrow{\mathrm{Pt}(g)} 4\mathrm{NO}(g) + 6\mathrm{H}_2\mathrm{O}(g)$$

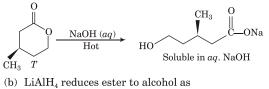
- (a, c) (a) Pure alumina does not electrolyse because it is a poor conductor of electricity and boils at 2000°C. While, melting point of pure aluminium is 1800°C. Thus, at 2000°C, Al gets vaporised.
  - (b) Roasting, not calcination of ore of copper is done in its extraction from chalcocite because CuS is to be converted into CuO and  $O_2$ . This is not used in calcination.
  - (c) Carbon can reduce CuO but does not reduce CaO because affinity of carbon for oxygen is greater than Cu and lesser than Ca.
  - $\begin{array}{ll} (d) \ SiO_2 \ is \ used \ to \ remove \ impurity \ of \ CaO \ present \\ in \ an \ ore. \quad CaO + SiO_2 \longrightarrow CaSiO_3 \\ & &$
- **8.** (c) (a) Hg<sup>+</sup> contains unpaired electron while Hg $_2^{2+}$  does not, so Hg<sup>+</sup> is paramagnetic while Hg $_2^{2+}$  is diamagnetic.
  - (b) Electron is not present in  $Th^{4+}$  for transition so,  $Th^{4+}$  is colourless.
  - (c) Zinc does not show variable valency because after the removal of both electrons from outer 4s-orbitals, completely filled *d*-subshell left  $(3d^{10})$ .
  - (d) La(OH)<sub>3</sub> is more basic than Lu(OH)<sub>3</sub> due to lanthanide contraction, Lu<sup>3+</sup> is smaller than La<sup>3+</sup>. So, Lu(OH)<sub>3</sub> is more covalent than La(OH)<sub>3</sub> and that is why basic character decreases from La(OH)<sub>3</sub> to Lu(OH)<sub>3</sub>.

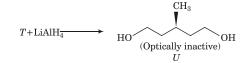
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It becomes optically inactive due to the formation of racemic mixture.

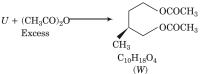
- **11.** (b, c, d) (a) Nylon-6, 6 is the polymer of adipic acid and hexamethylenediamine.
  - (b) Phenol formaldehyde resin (Resol or Novolac) is formed when the phenol/formaldehyde (P/F) ratio is greater than 1.
  - (c) Terylene or dacron is a condensation polymer because methanol or water released as a by product.
  - (d) Natural rubber is *cis*-rubber, i.e. it is the polymer of *cis*-isoprene, while synthetic rubber is the polymer of *trans*-isoprene.
- **12.** (b, d) (a) T undergoes an ester hydrolysis in hot aqueous alkali as





 ${}^{\prime}U{}^{\prime}$  does not have chiral carbon, thus, optically inactive.

(c) U on treatment with excess of acetic anhydride forms a diester as



(d) U on treatment with  $CrO_3$  /H<sup>+</sup> undergoes oxidation to diacid which gives efferve scence with NaHCO<sub>3</sub>.

$$U + \operatorname{CrO}_{3} \xrightarrow{H^{+}} \underbrace{\operatorname{CH}_{3}}^{O} \xrightarrow{O} \\ CH_{3} \xrightarrow{U} \\ U \xrightarrow{V} \xrightarrow{O} \\ CH_{3} \xrightarrow{V} \\ CH_{3} \xrightarrow{V} \\ CH_{3} \xrightarrow{O} \\ CH_{3} \xrightarrow$$

13. (a, c, d)

In neutral medium,

$$\begin{array}{c} \mathrm{MnO}_{4}^{-} \longrightarrow \mathrm{MnO}_{2}; (\mathrm{Mn}^{7+} + 3e^{-} \longrightarrow \mathrm{Mn}^{4+}) \\ \mathrm{In \ alkaline \ medium,} \\ \mathrm{MnO}_{4}^{-} \longrightarrow \mathrm{MnO}_{2}; (\mathrm{Mn}^{7+} + 3e^{-} \longrightarrow \mathrm{Mn}^{4+}) \\ \mathrm{In \ acidic \ medium,} \end{array}$$

 $\mathrm{MnO}_{4}^{-} \longrightarrow \mathrm{Mn}^{2+}; (\mathrm{Mn}^{7+} + 5e^{-} \longrightarrow \mathrm{Mn}^{2+})$ 

**14.** (3) Key Concept The groups change into the molecules are as follows

$$C = 0 \longrightarrow CO_{2}$$

$$2CH_{2}OH \longrightarrow 2CH_{2} = 0$$

$$3CHOH \longrightarrow 3HCOOH$$

$$HOH_{2}C \longrightarrow CH \longrightarrow CH \longrightarrow CH \longrightarrow CH_{2}OH$$

$$5HIO_{4} \longrightarrow OH \longrightarrow OH$$

$$3HCOOH + 2CH_{2} = 0 + CO_{2}$$

**15.** (1) In pure water only H<sup>+</sup> ion can be reduced for which  $2H^+ + 2e^- \longrightarrow H_2; E^\circ = 0.00V$ 

and according to question, *E* for the reduction at 1 atm pressure is – 0.414 V. Thus, according to Nernst's equation we can write

$$- 0.414 = 0 - \frac{0.0591}{2} \log \frac{[pH_2]}{[H^+]^2}$$
$$- 0.414 = -\frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$
$$\log [H^+] = -\frac{0.414}{0.0591} \approx - 7.00$$
$$[H^+] = 1.00 \times 10^{-7} M.$$

16. (5) For second order,

 $\Rightarrow$ 

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

Let a = 1

For 60% completion,  $k_2 = \frac{1}{30} \times \frac{0.6}{1(1-0.6)} = \frac{1}{30} \times \frac{0.6}{0.4}$ Now, for 20% completion,  $k_2 = \frac{1}{t} \times \frac{0.2}{1(1-0.2)} = \frac{1}{t} \times \frac{1}{4}$   $\therefore \quad k_2 \text{ is constant}$   $\therefore \quad \frac{1}{30} \times \frac{0.6}{0.4} = \frac{1}{t} \times \frac{1}{4}$   $\Rightarrow \qquad t = \frac{30}{0.6} \times \frac{0.4}{4} = 5 \text{ s}$  **17.** (3) For glucose solution,  $\Delta T_f = k_f \times m$  $k_f = \frac{0.186}{0.1} = 1.86 \text{ °C/molal}$ 

For propanoic acid solution,

$$\begin{split} \Delta T_{f}' &= k_{f} \times m \times i \\ i &= \frac{\Delta T_{f}'}{k_{f}m} = \frac{0.02046}{1.86 \times 0.01} = 1.1 \\ \text{C}_{2}\text{H}_{5}\text{COOH} \underbrace{\longrightarrow}_{\alpha} \text{C}_{2}\text{H}_{5}\text{COO}^{-} + \text{H}_{\alpha}^{+} \\ i &= 1 - \alpha + \alpha + \alpha = 1 + \alpha \\ \Rightarrow \quad 1.1 = 1 + \alpha \\ \therefore \qquad \alpha = 0.1 \\ \text{[H}^{+} \text{]} &= c\alpha = 0.01 \times 0.1 = 10^{-3} \\ \therefore \qquad \text{pH} = 3 \qquad [\because \text{pH} = -\log [\text{H}^{+}] \end{split}$$

**18.** (2) Key Concept Coordination isomerism occurs only in those complexes in which both cation and anion are complex.

It occurs due to exchange of ligands between cation and anion of complex spheres.

Here, among given complexes only two complexes, i.e.  $[Cr(NH_3)_6][Co(CN)_6]$  and  $[Cu(NH_3)_4][PtCl_6]$  show coordination isomerism.  $[Cr(NH_3)_6][Co(CN)_6] - [Co(NH_3)_6][Cr(CN)_6]$ 

$$[Cu(NH_3)_4][PtCl_6] - [Pt(NH_3)_4][CuCl_6]$$

**19.** (3)  
(i) 
$$R - C - R \xrightarrow{\text{Zn-Hg/HCl}}_{\text{Clemmensen's}} R - CH_2 - R$$
  
reduction  
(ii)  $R - C - R \xrightarrow{N_2H_2\overline{O}H}_{\text{Wolff-Kishner}} R - CH_2 - R$   
reduction  
(iii)  $R - C - R \xrightarrow{CH_2 - SH}_{\text{CH}_2 - SH} S - C - R \xrightarrow{H_2/Ni}_{\text{R} - CH_2 - R}$ 

**20.** (8) In dil. aq. H<sub>2</sub>SO<sub>4</sub>, the given complex is oxidised by MnO<sub>4</sub><sup>-</sup> which can be written as,

$$\frac{\text{MnO}_{4}^{-} + [\text{Fe}(\text{H}_{2}\text{O}) (\text{ox})_{2}]^{2^{-}} + 8\text{H}^{+} \rightarrow}{\text{Mn}^{2^{+}} + \text{Fe}^{3^{+}} + 4\text{CO}_{2} + 6\text{H}_{2}\text{O}}$$

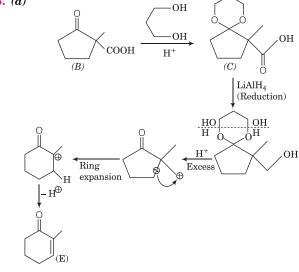
In this equation,

- ${\rm Fe}^{2+}$  is oxidised into  ${\rm Fe}^{3+}$
- Now,  $\frac{\text{Rate of change of } [\text{H}^+]}{\text{Rate of change of } [\text{MnO}_4^-]} = \frac{8}{1} = 8$

**21.** (9) Moles of solute,  $n_1 = \frac{w_1}{m_1}$ Moles of solvent,  $n_2 = \frac{w_2}{m_2}$ Mole fraction,  $\chi_1$  (solute) = 0.1 Mole fraction,  $\chi_2$  (solvent) = 0.9  $\therefore \qquad \frac{\chi_1}{\chi_2} = \frac{n_1}{n_2} = \frac{w_1}{m_1} \cdot \frac{m_2}{w_2} = \frac{1}{9}$ Molarity,  $m = \frac{\text{Solute (moles)}}{\text{Volume of solution (L)}} = \frac{w_1 \times 1000 \times 2}{m_1(w_1 + w_2)}$ Volume =  $\frac{\text{Total mass of solution}}{\text{Density}} = \left(\frac{w_1 + w_2}{2}\right) \text{mL}$ Molality,  $M = \frac{\text{Solute (moles)}}{\text{Volume of solvent (kg)}} = \frac{w_1 \times 1000}{m_1 \times w_2}$ Given, molarity = Molality  $\frac{1000}{100}w_1$  $2000 w_1$ Hence,  $m_1(w_1 + w_2)$  $m_1 w_2$  $\frac{w_2}{w_1 \,+\, w_2} = \frac{1}{2}$ *.*..  $\overline{2}$ Thus,  $w_1 = w_2 = 1$  $\frac{w_1m_2}{w_1m_2} = \frac{1}{1}$ *.*.. 9  $m_1 w_2$  $\frac{m_1 \; (\text{solute})}{m_2 \; (\text{solvent})}$ = 9 Thus,

**22.** (*d*) All reagents are used in haloform reaction, which convert (CH<sub>3</sub>CO) group followed by hydrolysis to give —COOH group.

**23**. (d)



**24.** (b)  $X_2(g) \rightleftharpoons 2X(g)$ At t = 0 1 0 At equilibrium  $\left(1 - \frac{x}{2}\right) = x$  (where,  $x = \beta_{eq}$ ) Total moles at equilibrium  $=\left(1 + \frac{x}{2}\right)$ 

Mole fractions, 
$$\chi_2(g) = \frac{\left(1 - \frac{x}{2}\right)}{\left(1 + \frac{x}{2}\right)}$$
  
 $\chi(g) = \frac{x}{1 + \frac{x}{2}} \text{ and } p = 2 \text{ bar}$   
Partial pressure  $(p_{\chi_2}) = \frac{1 - \frac{x}{2}}{1 + \frac{x}{2}} \cdot p$   
and  $p_{\chi} = \frac{p \cdot x}{\left(1 + \frac{x}{2}\right)}$   
 $\therefore \quad K_p = (p_{\chi})^2 / p_{\chi_2} = \frac{\left[px / \left(1 + \frac{x}{2}\right)\right]^2}{p \left(\frac{1 - \frac{x}{2}}{\left(1 + \frac{x}{2}\right)}\right]}$   
 $= \frac{4px^2}{4 - x^2} = \frac{8\beta_{eq}^2}{(4 - \beta_{eq}^2)}.$ 

**25.** (c) )(a)  $K_p = \frac{4p_{\chi^2}}{(4-x^2)} = px^2$  [:: 4>>> x]  $\therefore x \propto \sqrt{\frac{1}{p}}$ 

> If p decreases, x increases. Equilibrium gets shifted in the forward direction. Thus, statement (a) is correct.

(b) At the start of the reaction, Q = 0 where, Q is the reaction quotient.

$$\Delta G = \Delta G^{\circ} + 2.303 RT \log Q$$

Since,  $\Delta G^{\circ} < 0$ , thus  $\Delta G$  is – ve.

Hence, dissociation takes place spontaneously. Thus, (b) is correct.

(c) If we use 
$$x = 0.7$$
 and  $p = 2$  bar  
then  $K_p = \frac{4 \times 2(0.7)^2}{[4 - (0.7)^2]} = 1.11 > 1$ 

Thus, (c) is incorrect.

(d) At equilibrium, 
$$\Delta G = 0$$
  
 $\therefore \qquad \Delta G^{\circ} = -2.303 \ RT \ \log K_p$   
Since,  $\Delta G^{\circ} = + ve$   
Hence,  $K_p < 1$   
 $K_C = \frac{K_p}{(RT)}$   
 $\therefore \qquad K_C < 1$   
Thus, (d) is correct.

**26.** (a) Let, the heat capacity of insulated beaker be *C*. Mass of aqueous content in Exp.  $1 = (100 + 100) \times 1 = 200 \text{ g}$  $\Rightarrow$  Total heat capacity =  $(C + 200 \times 4.2)$  J/K Also, moles of acid-base neutralised in  $\begin{array}{l} \text{Exp. } 1=0.1\times 1=0.1\\ \Rightarrow \text{Heat released in Exp. } 1=0.1\times 57=5.7 \text{ kJ}\\ \Rightarrow \qquad 5.7\times 1000=-\left(C+200\times 4.2\right)\Delta T\\ \Rightarrow \qquad 5.7\times 1000=-\left(C+200\times 4.2\right)\times 5.7\\ \Rightarrow \qquad \left(C+200\times 4.2\right)=1000\\ \text{In 2nd Exp.} \qquad n_{\text{CH}_3\text{COOH}}=0.2 \text{, } n_{\text{NaOH}}=0.1\\ \text{Total mass of aqueous content}=200 \text{ g}\\ \Rightarrow \qquad \text{Total heat capacity}=\left(C+200\times 4.2\right)=1000\\ \Rightarrow \qquad \text{Heat released}=1000\times 5.6=5600 \text{ J}\\ \end{array}$ 

Overall only 0.1 mole of  $\rm CH_{3}COOH$  taking part in neutralisation.

$$\Rightarrow \quad \Delta H_{\text{neutralisation}} \text{ of } \text{CH}_{3} \text{COOH} = \frac{-5600}{0.1} = -56000 \text{ J/mol}$$

$$\Rightarrow \qquad \Delta H_{\text{ionisation}} \text{ of CH}_{3} \text{COOH} = 57 - 56 = 1 \text{ kJ/mol}$$

**27.** (b) 
$$pH = pK_a + \log \frac{|Salt_a|}{|acid_a|}$$

According to the formula of pH relating to  $pK_a$ .

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\Rightarrow pH = -\log[K_a] + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\Rightarrow pH = -\log(2 \times 10^{-5}) + \log \frac{0.1}{0.1}$$

$$\Rightarrow pH = 5 - \log 2 + 0$$

$$pH = 4.7$$

28. (b) Glucose forms osazone and is reducing in nature. Fructose also form osazone and is also reducing in nature. Lactose is also form osazone and is also reducing in nature. Sucrose is non-reducing compound. Starch is a polysaccharide and is non-reducing compound.

#### **29.** (b) Ore Formula

A. Siderite	$\rm FeCO_{3}$
B. Malachite	$CuCO_3 \cdot Cu(OH)_2$
C. Bauxite	AlO <sub>x</sub> (OH) <sub>3 - 2x</sub>
D. Calamine	ZnCO 3
E. Argentite	$Ag_2S$

Hence, the correct match is

 $A \to p,q,s \; ; \quad B \to t \; ; \quad C \to q, \; r \; ; \quad D \to r.$ 

**30.** (b) 
$$(CH_3)_2SiCl_2+H_2O \rightarrow (CH_3)_2Si(OH)_2+2HCl$$

$$\text{VCl}_5 + \text{H}_2\text{O} \longrightarrow \text{VOCl}_2 + 2\text{HCl}$$



# THERMODYNAMICS

#### A Collection of Best Asked Questions from JEE to Revise Your Concepts

- 1. The heats of combustion of carbon and<br/>carbon monoxide are -393.5 and -283.5 kJ mol<sup>-1</sup>,<br/>respectively. The heat of formation (in kJ) of carbon<br/>monoxide per mole is(a) 676.5(b) 676.5(c) 110.5(d) 110.5
- (c) Given,  $C(s) + O_2(g) \longrightarrow CO_2(g);$

$$\Delta H_1 = -393.5 \text{ kJ mol}^{-1} \dots (i)$$

$$\operatorname{CO}(g) + \frac{1}{2}\operatorname{O}_2(g) \longrightarrow \operatorname{CO}_2(g);$$

 $\Delta H_2 = -283.5 \text{ kJ mol}^{-1} \dots (\text{ii})$ 

We have to find enthalpy of formation of CO(g)

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta H = ?$$
 ...(iii)

By subtracting Eq. (ii) from Eq. (i), we get the required equation, i.e. Eq. (iii)  $% \left( \frac{1}{2} \right) = 0$ 

:. 
$$\Delta H = \Delta H_1 - \Delta H_2 = (-393.5 + 283.5) \text{ kJ mol}^{-1}$$
  
= - 110 kJ mol<sup>-1</sup>

- A reaction at 1 bar is non-spontaneous at low temperature but becomes spontaneous at high temperature. Identify the correct statement among the following.
   [JEE Main 2016]
  - (a) Both  $\Delta H$  and  $\Delta S$  are positive
  - (b)  $\Delta H$  is negative while  $\Delta S$  is positive
  - (c)  $\Delta H$  is positive while  $\Delta S$  is negative
  - (d) Both  $\Delta H$  and  $\Delta S$  are negative
- (a) Thinking Process Generally,  $\Delta H$  and  $\Delta S$  values do not change with temperature, but the magnitude of  $-T\Delta S$  term is dependent on temperature (*T*). For equivalent disorder, greater energy is absorbed at higher temperatures. Now for spontaneous process,  $\Delta G$  should be negative and for non-spontaneous process,  $\Delta G$  should be positive.

The relation among  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  and T is given as  $\Delta G = \Delta H - T \Delta S$ 

We have to check which option correctly shows both cases mentioned in the problem. Lets check them one by one.

For option (a) ( $\Delta H = +$  ve,  $\Delta S = +$  ve)

when temperature is low, the contribution of - $T\Delta S$  value is small and  $\Delta H$  predominates i.e.

$$\Delta H - T\Delta S > 0 \text{ or } \Delta G > 0$$

Thus, reaction is non-spontaneous.

When temperature is high,  $T \Delta S$  value increases and predominates over  $\Delta H$ 

i.e. 
$$\Delta H - T \Delta S < 0 \text{ or } \Delta G < 0$$

Thus, reaction is spontaneous.

Similarly, for option (d) ( $\Delta H = -ve$ ,  $\Delta S = -ve$ )

At low temperature,  $\Delta G < 0$ , reaction is spontaneous.

At high temperature,  $\Delta G > 0$ , reaction is non-spontaneous. For option (b) ( $\Delta H = -$  ve,  $\Delta S = +$  ve)

 $\Delta G$  comes out to be negative for both low as well as high temperatures

At low temperature  $\Delta H - T\Delta S < 0$ ;  $\Delta G < 0$ 

At high temperature  $\Delta H - T\Delta S < 0$ ;  $\Delta G < 0$ (-ve) (+ve)

For both cases  $-T\Delta S$  term comes out to be negative. Thus, reaction is spontaneous at both temperatures.

Similarly for option (c)  $\Delta G$  comes out to be positive at both low as well as high temperatures and reaction is non-spontaneous for both cases.

Since option (a), shows both cases mentioned in the problem, therefore, it is the correct option.

**3.** 1 mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ( $\Delta S_{surr}$ ) in JK<sup>-1</sup> is (1 L atm = 101.3 J) [IEE Advanced 2016]

$$\begin{array}{c} (a) \ 5.763 \\ (b) \ 1.013 \\ (c) - 1.013 \\ (d) - 5.763 \end{array}$$

(c) Key concept For isothermal process, change in internal energy is zero

i.e.  $\Delta U = nC_V \Delta T = 0 \qquad [\text{as } \Delta T = T_2 - T_1 = 0]$  According to first law of the thermodynamics,

$$\Delta U = q + w$$

$$q = -w$$

$$-q_{irrev} = w_{irrev} = p\Delta V$$

$$= 3(2 - 1) = 3 L \text{ atm}$$

#### 🔁 GOLDEN OLDIES

Also, 
$$\Delta S_{\text{surr}} = \frac{q_{\text{irrev}}}{T} = \frac{(-3 \times 101.3) \text{ J}}{300 \text{ K}}$$
  
 $= \frac{-303.9 \text{ J}}{300 \text{ K}} = -1.013 \text{ JK}^{-1}$ 

**4.** The following reaction is performed at 298 K,

$$2NO(g) + O_2(g) \Longrightarrow 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of  $NO_2(g)$  at 298 K?  $K_n = 1.6 \times 10^{12}$ [JEE Main 2015]  $\dot{(a)}\,R$ (298) l<br/>n $(1.6\times 10^{12})$  – 86600 (b) 86600 + R (298)  $\ln(1.6 \times 10^{12})$ (c) 86600 -  $\frac{\ln(1.6 \times 10^{12})}{\ln(1.6 \times 10^{12})}$ R(298)(d)  $0.5 [2 \times 86600 - R(298) \ln (1.6 \times 10^{12})]$ (d)  $\Delta G_f^{\circ} = \Delta G^{\circ}_{(\text{product})} - \Delta G^{\circ}_{(\text{reactant})}$  $= -RT \ln K_{n}$ Given,  $2NO(g) + O_2(g) \implies 2NO_2(g); K_p = 1.6 \times 10^{12}$ Also,  $\Delta G_f^{\circ}(NO) = 86.6 \text{ kJmol}^{-1} = 86,600 \text{ Jmol}^{-1}$ 

Now, we have,

$$\Delta G_f^{\circ} = 2\Delta G_{f(\mathrm{NO}_2)}^{\circ} - [2\Delta G_{f(\mathrm{NO})}^{\circ} + \Delta G_{f(\mathrm{O}_2)}^{\circ}]$$

or  $-RT \ln K_p = 2\Delta G_{f(NO_2)}^{\circ} - [2 \times 86,600 + 0]$ 

- $\Delta G_{f(\text{NO}_2)}^{\circ} = 0.5 \left[ 2 \times 86,600 R \times (298) \ln(1.6 \times 10^{12}) \right]$ *:*..
- **5.** For the process,  $H_2O(l) \longrightarrow H_2O(g)$

at  $T = 100^{\circ}$ C and 1 atm pressure, the correct choice is [JEE Advanced 2014] (a)  $\Delta S_{\rm sys} > 0$  and  $\Delta S_{\rm surr} > 0$  (b)  $\Delta S_{\rm sys} > 0$  and  $\Delta S_{\rm surr} < 0$ (c)  $\Delta S_{\rm sys}^{\rm sys} < 0$  and  $\Delta S_{\rm surr}^{\rm surr} > 0$  (d)  $\Delta S_{\rm sys}^{\rm sys} < 0$  and  $\Delta S_{\rm surr}^{\rm surr} < 0$ 

(b) Key concept The given problem is based on assumption  $(\mathfrak{d})$ that total entropy change of universe is zero.

i.e.  $\Delta S_{\text{universe}} = 0$ 

At 100°C and 1 atm pressure,

 $H_2O(l) \iff H_2O(g)$ 

For equilibrium,

$$\Delta S_{\text{total}} = 0$$

$$\Delta S_{\rm sys} + \Delta S_{\rm surr} = 0$$

Since, during conversion of liquid to gas entropy of system increases, in a similar manner entropy of surrounding decreases.

 $\Delta S_{\rm sys} > 0$  and  $\Delta S_{\rm surr} < 0$ ÷.

6. For the complete combustion of ethanol,

 $C_2H_5OH() + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O()$ , the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol<sup>-1</sup> at 25°C. Assuming ideality the enthalpy of combustion,  $\Delta_C H$ , for the reaction will be  $(R = 8.314 \,\text{JK}^{-1} \,\text{mol}^{-1})$  [JEE Main 2014]  $(a) - 1366.95 \, \rm kJ \ mol^{-1}$  $(b) - 1361.95 \text{ kJ mol}^{-1}$  $(c) - 1460.50 \ \rm kJ \ mol^{-1}$  $(d) - 1350.50 \text{ kJ mol}^{-1}$ 

(a) For the given reaction,  

$$C_{2}H_{5}OH(l) + 3O_{2}(g) \longrightarrow 2CO_{2}(g) + 3H_{2}O(l)$$

$$\Delta U = -1364.47 \text{ kJ mol}^{-1}$$

$$\Delta H = \Delta U + \Delta n_{g}RT$$

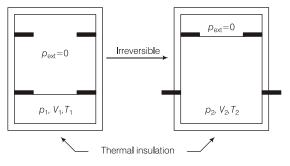
$$\Delta n_{g} = 2 - 3 = -1$$
∴ 
$$\Delta H = -1364.47 + (-1) \times 0.008314 \times 298$$

$$= (-1364.47 - 2.4776) \text{ kJ mol}^{-1}$$

$$= -1366.95 \text{ kJ mol}^{-1}$$

7. An ideal gas in thermally insulated vessel at internal pressure =  $p_1$ , volume =  $V_1$  and absolute temperature =  $T_1$  expands irreversibly against zero external pressure, as shown in the diagram.

The final internal pressure, volume and absolute temperature of the gas are  $p_2$ ,  $V_2$  and  $T_2$ , respectively. For this expansion [JEE Advanced 2014]



$$\begin{array}{ll} (a) \ q = 0 & (b) \ T_2 = T_1 \\ (c) \ p_2 V_2 = \ p_1 V_1 & (d) \ p_2 V_2^\gamma = \ p_1 V_1^\gamma \end{array}$$

(a,b,c) Key concept This question includes concept of isothermal adiabatic irreversible expansion. Process is adiabatic because of the use of thermal insulation therefore, q = 0

$$\begin{split} w &= p_{\text{ext}} \cdot \Delta V \\ &= 0 \times \Delta V = 0 \end{split} \qquad \qquad [\because p_{\text{ext}} = 0] \end{split}$$

Internal energy  $(\Delta U)$  is given by

$$\Delta U = q + w = 0$$

The change in internal energy of an ideal gas depends only on temperature.

 $\Delta T = 0$ [isothermal process]  $T_{2} = T_{1}$ or,

$$p_2 V_2 = p_1 V_2$$

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 $p_2 V_2^{\gamma} = p_1 V_1^{\gamma}$  is valid for adiabatic reversible process.

8. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be  $(R = 8.314 \text{ J/mol K}, \ln 7.5 = 2.01)$ [IEE Main 2013]

(a) 
$$q = +208 \text{ J}, W = -208 \text{ J}$$
  
(b)  $q = -208 \text{ J}, W = -208 \text{ J}$   
(c)  $q = -208 \text{ J}, W = +208 \text{ J}$   
(d)  $q = +208 \text{ J}, W = +208 \text{ J}$ 



(a) Key concept For isothermal expansion process

 $q = -W, \Delta E = 0$  $W = -nRT \ln \frac{V_2}{V_1}$ 

Given,

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$$n = 0.04$$
 mole,  
 $T = (37 + 273)$  K = 310 K,

 $V_1 = 50 \text{ mL}, V_2 = 375 \text{ mL}$ 

$$W = -0.04 \times 8.314 \times 310 \ln \frac{57}{50}$$
  
 $a = +208 \text{ J}$ 

$$W = -208 \text{ J}$$
 [expansion work]

- 9. The standard enthalpies of formation of CO<sub>2</sub>(g), H<sub>2</sub>O(l) and glucose (s) at 25°C are 400 kJ/mol, 300 kJ/mol and 1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is [JEE Advanced 2013] (a) + 2900 kJ (b) 2900 kJ (c) 16.11 kJ (d) + 16.11 kJ
- (c) Key concept Standard heat of combustion ( $\Delta_c H^\circ$ ) is the standard enthalpy change, when one mole of the substance is completely oxidised.

$$\begin{split} \text{Given,} \quad & \Delta_f H^{\circ}(\text{CO}_2) = -\ 400\ \text{kJ}\ \text{mol}^{-1} \\ & \Delta_f H^{\circ}(\text{H}_2\text{O}) = -\ 300\ \text{kJ}\ \text{mol}^{-1} \\ & \Delta_f H^{\circ}(\text{glucose}) = -\ 1300\ \text{kJ}\ \text{mol}^{-1} \\ & \Delta_f H^{\circ}(\text{O}_2) = 0 \\ & \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) +\ 6\text{O}_2(g) \longrightarrow 6\text{CO}_2(g) +\ 6\text{H}_2\text{O}(l) \\ & \Delta_C H^{\circ}(\text{glucose}) = 6[\Delta_f H^{\circ}(\text{CO}_2) +\ \Delta_f H^{\circ}(\text{H}_2\text{O})] \\ & -\ [\Delta_f H^{\circ}(\text{C}_6\text{H}_{12}\text{O}_6) +\ 6\Delta_f H^{\circ}(\text{O}_2)] \\ & = 6\ (-\ 400 -\ 300) - (-\ 1300 +\ 6\times 0) \\ \end{split}$$

 $= -2900 \text{ kJ mol}^{-1}$ 

- Molar mass of  $C_6 H_{12} O_6 = 180 \text{ g mol}^{-1}$
- $\therefore$  Standard heat of combustion of glucose per gram

$$= \frac{-2900 \text{ kJ mol}^{-1}}{180 \text{ g mol}^{-1}} = -16.11 \text{ kJ g}^{-1}$$

10. Using the data provided, calculate the multiple bond energy (kJ mol<sup>-1</sup>) of a C≡C bond in C<sub>2</sub>H<sub>2</sub>. That energy is (take the bond energy of a C—H bond as 350 kJ mol<sup>-1</sup>)

② (d) Key concept For calculation of C == C bond energy, first calculate dissociation energy of  $C_2H_2$ .

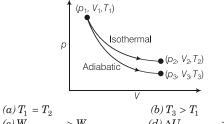
$$C_2H_2(g) \longrightarrow 2C(g) + 2H(g); \Delta H = ?$$
 ...(i)

Given, 
$$C_2H_2(g) \longrightarrow 2C(g) + 2H(g); \Delta H_1 = -225 \text{ kJ} \dots (ii)$$
  
 $2C(g) \longrightarrow 2C(g): \Delta H_2 = 1410 \text{ kJ} \dots (iii)$ 

$$H_2(g) \longrightarrow 2H(g); \Delta H_3 = 330 \text{ kJ} \qquad \dots (iv)$$

$$\begin{split} \Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -225 + 1410 + 330 = 1515 \, \text{kJ} \\ \Delta H &= 2\text{BE}_{(\text{C}-\text{H})} + \text{BE}_{(\text{C}=\text{C})} \\ 1515 &= 2 \times 350 + \text{BE}_{(\text{C}=\text{C})} \\ \text{BE}_{(\text{C}=\text{C})} &= 1515 - 700 = 815 \, \text{kJ} \, \text{mol}^{-1} \end{split}$$

 11. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?

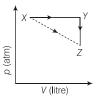


- (c) W<sub>isothermal</sub> > W<sub>adiabatic</sub>
   (d) ΔU<sub>isothermal</sub> > ΔU<sub>adiabatic</sub>
   (a, c, d) Change of state (p<sub>1</sub>, V<sub>1</sub>, T<sub>1</sub>) to state (p<sub>2</sub>, V<sub>2</sub>, T<sub>2</sub>) is an isothermal expansion therefore, T<sub>1</sub> = T<sub>2</sub>
  - Change of state  $(p_1, V_1, T_1)$  to state  $(p_3, V_3, T_3)$  is an adiabatic expansion it brings cooling of gas therefore,  $T_3 < T_1$ .

Work done in the area under the curve of p - V diagram.

$$\begin{split} W_{\rm isothermal} &> W_{\rm adiabatic} \\ \Delta U &= n C_V \Delta T \\ \Delta U &= 0 \text{ as } \Delta T = 0 \qquad (\text{isothermal process}) \\ \Delta U &= n C_V (T_3 - T_1) < 0 \text{ as } T_3 < T_1 \text{ (adiabatic process)} \\ \Rightarrow \quad \Delta U_{\rm isothermal} > \Delta U_{\rm adiabatic} \end{split}$$

**12.** For an ideal gas, consider only p - V work in going from initial state *X* to the final state *Z*. The final state *Z* can be reached by either of the two paths shown in the figure.



[Take  $\Delta S$  as change in entropy and *W* as work done]. Which of the following choice(s) is (are) correct?

[JEE Main 2012]

$$\begin{array}{l} & (a) \Delta S_{X \to Z} = \Delta S_{X \to Y} + \Delta S_{Y \to Z} \\ & (b) W_{X \to Z} = W_{X \to Y} + W_{Y \to Z} \\ & (c) W_{X \to Y \to Z} = W_{X \to Y} \\ & (d) \Delta S_{X \to Y \to Z} = \Delta S_{X \to Y} \end{array}$$

(a, c) Key concept Entropy is a state function and change in entropy in a cyclic process is zero.

Work is a path function, i.e. it depends upon the path followed.

$$\begin{array}{l} \Delta S_{X \ \rightarrow \ Y} + \Delta S_{Y \rightarrow Z} + \Delta S_{Z \rightarrow X} = 0 \\ - \ S_{Z \ \rightarrow \ X} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z} \end{array}$$

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 $\Delta S_{X \to Z} = \Delta S_{X \to Y} + \Delta S_{Y \to Z} \quad [\therefore \Delta S_{X \to Z} = -\Delta S_{Z \to X}]$ or

$$W_{Y \to Z} = 0 \text{ as } \Delta V = 0$$

$$W_{X \to Y \to Z} = W_{X \to Y}$$

Also, work is the area under the curve on p - V diagram  $W_{X \to Y} + W_{Y \to Z} + W_{X \to Y} = W_{X \to Y \to Z}$ 

- **13.** The bond energy (in kcal  $mol^{-1}$ ) of C—C single bond is approximately [IEE Main 2010] (a) 1*(b)* 10 (c) 100(d) 1000
- $\bigcirc$  (c) The bond energy of C C single bond is approximately 100 kcal.
- **14.** The species which by definition has zero standard molar enthalpy of formation at 298 K is IFF Main 2010

			JEE Main 201
$(a)\operatorname{Br}_2(g)$	$(b)\operatorname{Cl}_2(g)$	(c) H <sub>2</sub> O $(g)$	$(d) \operatorname{CH}_4(g)$

- (b) Elements in its standard state have zero enthalpy of formation.  $\mathrm{Cl}_2$  is gas at room temperature, therefore.  $\Delta H_f^\circ$  of  $\operatorname{Cl}_2(g)$  is zero.
- **15.** Among the following extensive property is (properties are) [JEE Main 2010] (a) molar conductivity (b) electromotive force
  - (c) resistance
  - (d) heat capacity
- (c, d) Key concept Extensive properties are mass dependent while intensive properties are mass independent. Resistance and heat capacity are mass dependent properties, hence they are extensive.
- **16.** Among the following, the state function(s) is(are) [JEE Main 2009]
  - (a) internal energy
  - (b) irreversible expansion work
  - (c) reversible expansion work
  - (d) molar enthalpy

(**a**)

- (a, c, d) Key concept State function is independent to the  $\odot$ way in which the state is attained, i.e. path independent. Internal energy, molar enthalpy are state functions. Also, reversible expansion work is a state function because between given initial and final states, there can be only one reversible path.
- **17.** The value of  $\log_{10} K$  for a reaction,  $A \Longrightarrow B$  is

$$\begin{array}{l} (\text{Given, } \Delta_r H_{298\ \text{K}}^{\circ} = -\ 5407\ \text{kJ\ mol}^{-1}), \\ \Delta_r S_{298\ \text{K}}^{\circ} = 10\ \text{J}\text{K}^{-1}\text{mol}^{-1}\ \text{and}\ R = 8.314\ \text{J}\text{K}^{-1}\text{mol}^{-1}, \\ 2.303 \times 8.314 \times 298 = 5705 \qquad \text{[JEE\ Main\ 2007]} \\ (a)\ 5 \qquad (b)\ 10 \qquad (c)\ 95 \qquad (d)\ 100 \\ \hline \textbf{(b)}\ \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \\ & = -\ (54.07 \times 10^3)\ \text{J} - (298 \times 10)\ \text{J} \\ & = -\ 57.05 \times 10^3\ \text{J} \\ \text{Also,} \qquad \Delta G^{\circ} = -\ 2.303RT\ \log\ K \\ \text{or,} \qquad \log\ K = \frac{-\ \Delta G^{\circ}}{2.303RT} = \frac{57.05 \times 10^3}{5705} = 10 \end{array}$$

**18.** For the process 
$$H_2O(l)$$
 (1 bar, 373 K)  $\rightarrow$   $H_2O(g)$   
(1 bar, 373 K), the correct set of thermodynamic  
parameters is [JEE Main 2007]  
(a)  $\Delta G = 0$ ,  $\Delta S = +$  ve  
(b)  $\Delta G = 0$ ,  $\Delta S = -$  ve  
(c)  $\Delta G = +$  ve,  $\Delta S = 0$ 

(d)  $\Delta G = -$  ve,  $\Delta S = +$  ve

- (a) At transition point, i.e. 373 K and 1 bar, liquid remains  $(\mathfrak{d})$ in equilibrium with vapour phase, therefore  $\Delta G = 0$ . As vaporisation occurs, degree of randomness increases, hence  $\Delta S > 0$ , i.e.  $\Delta S = +$  ve.
- **19.** The direct conversion of *A* to *B* is difficult, hence it is carried out by the following shown path

$$C \longrightarrow D$$

$$A \longrightarrow B$$

$$\Delta S_{(A \to C)} = 50 \text{ eu}$$

$$\Delta S_{(C \to D)} = 30 \text{ eu}$$

$$\Delta S_{(D \to B)} = -20 \text{ eu}$$

where, eu is entropy unit

Given that,

Then, $\Delta S_{(A \rightarrow B)}$ is		[JEE Main 2006]
$(a) + 100 \mathrm{eu}$	(b) + 60 eu	
(c) – 100 eu	( <i>d</i> ) – 60 eu	

(b) Entropy is a state function hence,  $\Delta S_{A \to B} = \Delta S_{A \to C} + \Delta S_{C \to D} + \Delta S_{D \to B}$ 

$$= 50 \text{ eu} + 30 \text{ eu} + (-20) \text{ eu} = 60 \text{ eu}$$

**20.** A monoatomic ideal gas undergoes a process in which the ratio of *p* to *V* at any instant is constant and equals to 1. What is the molar heat capacity of [IEE Main 2006] the gas?

(a) 
$$\frac{4R}{2}$$
 (b)  $\frac{3R}{2}$  (c)  $\frac{5R}{2}$  (d) 0

(a) Given, 
$$\frac{p}{V} = 1 \Rightarrow p = V$$
 or  $dp = dV$  ...(i)

Also, from first law of thermodynamics

$$dq = C_V dT + p dV \qquad \dots (ii)$$

For one mole of an ideal gas, pV = RTndV + Vdn = RdT...(iii)

$$pav + vap = har$$

From Eq. (i), pdV = VdpSubstituting pdV = Vdp in Eq. (iii), we get

$$2pdV = RdT$$

or 
$$pdV = \frac{R}{2}dT$$

Now, from Eq. (ii),

$$\Rightarrow \qquad dq = C_V dT + \frac{R}{2} dT$$

For monoatomic gas

$$C_V = \frac{3}{2}R$$

$$\Rightarrow \qquad \frac{dq}{dT} = C_V + \frac{R}{2} = \frac{3}{2}R + \frac{R}{2} = 2R$$



# ASSERTION & REASON ZONE

A Practice Set of Best Assertion and Reason Problems for Medical Entrances from Complete Syllabus

**Directions (Q. Nos. 1-30)** In the following questions a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

- (a) Both Assertion and Reason are true and Reason is the correct explanation of the Assertion
- (b) Both Assertion and Reason are true but Reason is not the correct explanation of the Assertion
- (c) Assertion is true but Reason is false
- (d) Both Assertion and Reason are false
- Assertion (A) Mischmetal is used in making a magnesium based alloy.
   Reason (R) It is a pyrophoric alloy.
- 2. Assertion (A) Na<sup>+</sup> and Al<sup>3+</sup> are isoelectronic but the magnitude of ionic radius of Al<sup>3+</sup> is less than that of Na<sup>+</sup>.

**Reason** (R) The magnitude of effective nuclear charge of outer shell electrons in  $Al^{3+}$  is greater than that in Na<sup>+</sup>.

**3.** Assertion (A) F—N—F bond angle in NF<sub>3</sub> is 102° 30′, while H—N—H bond angle in NH<sub>3</sub> is 107°48′. **Reason** (R) Repulsion between bond pair electrons is more in NF<sub>3</sub> than NH<sub>3</sub>.

**4.** Assertion (A) The time period of revolution of an electron moving in second orbit of He<sup>+</sup> is two times larger than the time period of an electron moving in first orbit of hydrogen.

**Reason** (R) Kinetic energy of an electron moving in nth Bohr's orbit is directly proportional to second power of n.

- **5.** Assertion (A) Addition of HBr to 1-butene gives two optical isomers.
   **Reason** (R) 1-butene is unsymmetrical in nature.
- **6. Assertion** (A) When an atom crystallises in hcp or fcc arrangement, density of the solid remains same in both the arrangements.

**Reason** (R) Both hcp and fcc have same value of limiting packing fractions.

**7. Assertion** (A) When a mixture of sodium sulphite and sodium arsenite is exposed to air, the oxidation reaction of sodium sulphite induces the oxidation of sodium arsenite by air.

**Reason** (R) Sodium sulphite solution is oxidised by air but sodium arsenite is not.

**8. Assertion** (A) On dilution, the equivalent as well as molar conductivity of solution increases.

**Reason** (R) With dilution, the number of current carrying particles per cm<sup>3</sup> increases. [AIIMS 2009]

**9.** Assertion (A) In the decomposition of  $N_2O_5$ , the time taken to reduce the concentration of  $N_2O_5$  half of the original amount is 12 min at 50°C, while 5h at 25°C and 10 days at 0°C.

**Reason** (R) For a chemical reaction, with rise in temperature by 10°C, the rate constant nearly tripled.

 10. Assertion (A) Sodium-2-dodecyl benzene sulphonate is a biodegradable detergent.
 Reason (R) Detergents having highly branched chains are biodegradable.

## AIIMS CAPSULE

**11. Assertion** (A) When double or triple bond is formed, the bond length decreases and bond energy increases.

**Reason** (R) Greater the overlapping, larger is the attraction between nuclei.

- **12.** Assertion (A) The value of  $K_C$  for the reaction,  $2A \Longrightarrow B + C$  is  $2 \times 10^{-3}$ . At a given time, the composition of reaction mixture is [A] = [B] = [C]  $= 3 \times 10^{-4}$  M, then the reaction proceeds in the reverse direction. **Reason** (R)  $Q_C > K_C$  for the above reaction.
- **13.** Assertion (A)  $K_4[Fe(CN)_6]$  is diamagnetic and  $K_3[Fe(CN)_6]$  is paramagnetic. **Reason** (R) Hybridisation of central metal in  $K_3[Fe(CN)_6]$  and in  $K_4[Fe(CN)_6]$  is  $d^2sp^3$ .
- **14.** Assertion (A) Basicity of  $CH_3CH_2NH_2(I)$ ,  $NH_3(II)$ and  $C_6H_5NH_2$  (III) is in the order I > II > III. **Reason** (R) Electron-donating groups (such as alkyl group) increase the basicity of amines and electronwithdrawing groups (such as aryl group) decrease the basicity of amines.
- **15.** Assertion (A)  $HPO_4^{2-}$ ,  $HCO_3^{-}$ ,  $HSO_4^{-}$ ,  $H_2PO_4^{-}$  and  $H_2PO_3^{-}$  are amphoteric.

 $\ensuremath{\textbf{Reason}}$  (R) They act as proton acceptor as well as proton donor.

**16.** Assertion (A) A gaseous reaction with negative enthalpy and positive entropy is spontaneous at any temperature.

**Reason** (R) For a reaction to be spontaneous, the Gibbs free energy should always be positive.

**17. Assertion** (A) Electroneutrality principle is a simple consequence of the thermodynamic work required to separate the opposite charges or to bring like charges into closer contact.

**Reason** (R) The additional work raises the free energy  $(\Delta G)$  of the process, making it more spontaneous.

**18. Assertion** (A) 8 : 8 coordination number of CsCl at low temperature changes to 6 : 6 coordination number at high temperature.

**Reason** (R) Temperature influences the structure of solids.

- **19. Assertion** (A) The number of alkyl groups attached to positively charged carbon increases, the stability of carbocation. **Reason** (R) This is due to inductive and hyperconjugative effects.
- **20. Assertion** (A) Alkynes are more reactive towards nucleophilic addition reaction as compared to alkenes.

**Reason** (R) Alkynes contain two  $\pi$  bonds, while alkenes have only one  $\pi$  bond.

**21. Assertion** (A) Colloidal state of matter is a state in which the size of the particles is such that they can pass through filter paper.

**Reason** (R) Their particle size is more than  $10^{-6}$  m or 1000 nm.

**22. Assertion** (A) The metals of group IInd form ionic compounds (except Be).

**Reason** (R) The reducing character and electropositive character increase down the group.

**23. Assertion** (A) The electron affinity of chlorine is greater than fluorine.

**Reason** (R) Fluorine has small size, as a result of which strong electron-electron repulsion are present in relatively compact 2*p*-orbitals of fluorine.

**24.** Assertion (A)  $PF_3$  obeys octet rule but  $PF_5$  does not.

**Reason** (R) 3d-orbitals play crucial role during formation of  $PF_5$ .

**25. Assertion** (A) In the analysis of group IV, cations are precipitated as their sulphides.

 $\mbox{Reason}\ (R)$  For precipitation high concentration of  $S^{2-}$  is required.

**26. Assertion** (A) 2-bromopentane, when treated with alcoholic KOH, yields a mixture of three alkenes *A*, *B* and *C*.

2-bromopentane  $\xrightarrow{\text{Alc. KOH}}$  1-pentene + *cis*-2-pentene A B+ *trans*- 2-pentene

C

**Reason** (R) The reaction proceeds through E2 mechanism and product *B* is predominant.

**27. Assertion** (A) Alcohols are dehydrated to hydrocarbons in the presence of acidic zeolites.

**Reason** (R) Zeolites are porous catalysts.

**28.** Assertion (A) The coagulating power of an electrolyte for arsenious sulphide sol decreases in the order  $Na^+ > Al^{3+} > Ba^{2+}$ .

**Reason** (R) According to Hardy-Schulze rule, coagulating power of an electrolyte is inversely proportional to the valency of active ions.

29. Assertion (A) Brady's reagent is 2, 4-DNP.Reason (R) It react with — OH group of the

**Reason** (R) It react with — OH group of the compounds to form a yellow precipitate.

**30.** Assertion (A) 1,3-butadiene is the monomer for natural rubber.

**Reason** (R) Natural rubber is formed through anionic addition polymerisation.

## Answers with Explanation

- **1.** (b) Mischmetal is used in making a magnesium based alloy because when Mg is mixed with about 3% misch metal, it increases the strength of Mg.
- **2.** (a)  $\operatorname{Na}^+ = [\operatorname{Ne}]3s^0$ ;  $\operatorname{Al}^{3+} = [\operatorname{Ne}]3s^0$

The number of valence electrons in  $Na^+$  and  $Al^{3+}$  are same. Hence, they are isoelectronic.

The magnitude of ionic radius of  $Al^{3+}$  is less than  $Na^+$  because the magnitude of effective nuclear charge of  $Al^{3+}$  is greater than that in  $Na^+$ .

- **3.** (c) Due to high electronegativity of F, it pulls the bonding electrons farther away from N than H, in  $NH_3$ . Hence, repulsion between bond pair electrons is less in  $NF_3$  than in  $NH_3$  and the lone pair in  $NF_3$  causes a greater distortion from tetrahedral geometry and gives a F—N—F bond angle of 102°30′ compared with 107°48′ in  $NH_3$ .
- **4.** (c) The time period and kinetic energy of an electron moving in *n*th Bohr's orbit are given by

$$T = \frac{n^{3}h^{3}}{4\pi^{2}mK^{2}Z^{2}e^{4}} \text{ or } T \propto \frac{n^{3}}{Z^{2}}$$
$$\text{KE} = \frac{2\pi^{2}mK^{2}Z^{2}e^{4}}{n^{2}h^{2}} \text{ or } \text{KE} \propto \frac{Z^{2}}{n^{2}}$$

and

Hence, kinetic energy is inversely proportional to second power of n.

Also, T for second orbit of He<sup>+</sup> =  $\frac{2h^3}{4\pi^2 m K^2 Z^2 e^4}$ 

Which is two times the time period of first orbit of hydrogen. Hence, assertion is correct but reason is incorrect.

**5.** (a) In the addition reaction of butene with Hydrogen bromide, two isomeric products are obtained, it is due to unsymmetrical nature of butene.

 $+ \operatorname{CH}_3 \operatorname{CH}_2 \operatorname{CHBrCH}_3 \\ \text{2-bromobutane (Optically active)}$ 

In the above isomeric products 2-bromobutane contains one asymmetrical carbon (n = 1) hence there are  $2^n = 2$ optical isomers.

- (a) This is the phenomenon of induced oxidation. Reactions involving in this phenomenon are given as Na<sub>2</sub>SO<sub>3</sub> + O<sub>2</sub> → Na<sub>2</sub>SO<sub>5</sub> Na<sub>2</sub>SO<sub>2</sub> + Na<sub>2</sub>AsO<sub>2</sub> → Na<sub>2</sub>AsO<sub>4</sub> + Na<sub>2</sub>SO

$$\frac{1}{\text{Na}_2\text{SO}_5 + \text{Na}_3\text{AsO}_3 \longrightarrow \text{Na}_3\text{AsO}_4 + \text{Na}_2\text{SO}_4}{\text{Na}_2\text{SO}_3 + \text{Na}_3\text{AsO}_3 + \text{O}_2 \longrightarrow \text{Na}_3\text{AsO}_4 + \text{Na}_2\text{SO}_4}$$

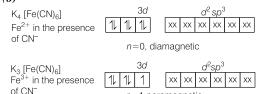
- **8**. *(c)* On dilution, the inter-ionic attractions decrease thus, equivalent as well as molar conductivities increase. However, the number of current carrying particles per cm<sup>3</sup> decrease on diluting the solution.
- **9.** (c) Generally, for a chemical reaction, with rise in temperature by 10°C, the rate constant nearly doubled.
- **10.** (*d*) Detergents with straight chains (unbranched chains) are biodegradable. Since, sodium-2-dodecylbenzene sulphonate has branched chain, it is a non-biodegradable detergent.

- **11.** (a) Both assertion and reasons are true and reason is the correct explanation of the assertion.
- **12.** (a) For the reaction, the reaction quotient  $Q_C$  is given by

$$egin{aligned} Q_C &= [B][C] \, / \, [A]^2 \ [A] &= [B] = [C] = 3 imes 10^{-4} \ \mathrm{M} \ Q_C &= rac{(3 imes 10^{-4})(3 imes 10^{-4})}{(3 imes 10^{-4})^2} = 1 \end{aligned}$$

As  $Q_{\rm C} > K_{\rm C},$  so the reaction will proceed in the reverse direction.

as



- **14.** (*a*) Both assertion and reason are true and reason is the correct explanation of the assertion.
- **15.** (*a*) Both assertion and reason are correct and reason is the correct explanation of the assertion.

n=1 paramagnetic

- **16.** (*c*) For a reaction to be spontaneous, the Gibbs free energy should always be negative. The feasibility of a reaction can be calculated from the relation  $\Delta G = \Delta H T \Delta S$ .
- **17.** (c) The additional work raises the free energy  $(\Delta G)$  of the process and making it less spontaneous.
- **18.** (*a*) On heating to 760 K, CsCl changes to NaCl structure, i.e. at high temperature coordination number decreases.
- **19.** (*a*) The number of alkyl groups attached to positively charged carbon increase the stability of carbocation due to inductive and hyperconjugative effect. Thus, the order of stability of carbocation is  $CH_3^+ < CH_3CH_2^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$ .
- **20.** (*b*) The nucleophilic addition reaction of alkynes is given

$$-\underbrace{C=C-+Nu}^{\ominus} \longrightarrow Nu-C=C^{\ominus}$$
 A vinyl carbanion

The possible reaction with alkene will be as

The negative charge on vinyl carbanion is on  $sp^2$  carbon and that on alkyl carbocation is on  $sp^3$  carbon. The negative charge is more stabilised at  $sp^2$ -carbon than  $sp^3$ -carbon atom or we can say that vinyl carbanion is more stable than alkyl carbanion.

- **21.** (c) Their particle size is between  $10^{-9}$  to  $10^{-6}$  m or 1 nm to 1000 nm.
- **22.** (*a*) Both assertion and reason are correct and reason is the correct explanation of the assertion.

*To be Continued at Page 78* 

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- Electrochemistry is a branch of chemistry that deals with interconversion of chemical energy and electrical energy.
- It is the study of electron flow within redox reactions, i.e. the relationship between electricity and chemical changes.

## **1** ELECTROLYSIS

- (i) It is a process in which electric current is used to bring a chemical change.
- (ii) It is done in an electrolytic cell.
- (iii) Infact, electric current is used to bring a non-spontaneous chemical reaction (the reaction for which  $\Delta G = +$  ve and  $E_{cell} = +$  ve)

#### FARADAY'S LAWS OF ELECTROLYSIS

#### (I) FARADAY'S FIRST LAW

When electric current is passed through an electrolytic solution, the amount of substance deposited at electrodes (w) is directly proportional to the electric charge passed

$$\propto 0$$
 or  $w = Zit$ ;  $(0 = it)$ 

Z = electrochemical equivalent, depends on the nature of substance deposited.

#### (II) FARADAY'S SECOND LAW

When same amount of current is passed through different electrolytic solutions, the mass of substance (w) deposited at respective electrodes is directly proportional to equivalent weight (E).

$$w \propto E \text{ or } \frac{w_1}{w_2} = \frac{E_1}{E_2}$$

If Q = 96500 C, w = E,

So, 
$$E = 96500 Z$$
 (from 1st law)

or 
$$w = \frac{EQ}{96500} = \frac{Eit}{96500}$$
 (from 2nd law)

#### PREFERENTIAL DISCHARGE OF IONS

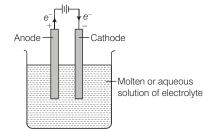
During electrolysis, if more than one type of positive or negative ions are present, only one ion is discharged in preference to other. The order of preference is **Cations**  $K^+ > Ca^{2+} > Na^+ > Mg^{2+} > Al^{3+} >$   $Zn^{2+} > Fe^{2+} > Sn^{2+} > Pb^{2+} > H^+ > Cu^{2+} >$  $Hg^{2+} > Ag^+ > Au^{3+}$ 

Anions  $SO_4^2 > NO_3^- > OH^- > Cl^- > Br^- > I^-$ 

#### APPLICATIONS OF ELECTROLYSIS

- Metals like Na, Mg, Al and K are obtained by the electrolysis of their fused salts.
- Refining of metals like Ag, Au, Cu etc., by electrolysis.
  Coating of an inferior metal (cathode) by a superior
- metal (anode) called **electroplating**.

#### ELECTROLYTIC CELL



- It is used to bring chemical change by passing electricity through electrolytic solution.
- In this cell ions are discharged at both the electrodes.
- Flow of current (i.e. electrons) occurs through the wire.

## **2** CONDUCTANCE OF ELECTROLYTIC SOLUTION

The conductance (G) of an electrolytic solution is measured by determining the resistance of the solution in a conductivity cell between two flat or cylindrical electrodes separated by a fixed distance.

:. Conductance =  $\frac{1}{\text{Resistance}}$ 

i.e. conductance is the ease of flow of electrons.

#### e. conductance is the case of now of electrons

## **TYPES OF CONDUCTANCE**

(I) SPECIFIC CONDUCTANCE (κ)

t is the reciprocal of specific resistance (
$$\rho$$
).  $\kappa = \frac{l}{A} \times C$   
where,  $C = \frac{1}{R} = \text{conductance}; \frac{l}{A} = \text{cell constant.}$ 

Unit = s m<sup>$$-1$$</sup> or s cm <sup>$-1$</sup> 

I

#### (II) EQUIVALENT CONDUCTANCE ( $\Lambda$ )

The conductance of all ions produced by one gram equivalent of an electrolyte. If volume of solution containing 1 g-eq is VmL, then

$$\Lambda = \kappa \times V_{\rm mL} = \kappa \times \frac{1000}{N}$$

Unit = s cm<sup>2</sup>eq<sup>-1</sup> or  $\Omega^{-1}$  cm<sup>2</sup>eq<sup>-1</sup> or  $\Omega^{-1}$ m<sup>2</sup>eq<sup>-1</sup>

## (III) MOLAR CONDUCTANCE ( $\Lambda_m$ )

The conductance of all ions produced by one gram mole of an 1000

electrolyte. 
$$\Lambda_{\rm m} = \kappa \times V_{\rm mL} = \kappa \times \frac{1}{M}$$
  
Unit = s cm<sup>2</sup>mol<sup>-1</sup> or  $\Omega^{-1}$  cm<sup>2</sup>mol<sup>-1</sup> or  $\Omega^{-1}$  m<sup>2</sup>mol<sup>-1</sup>

Note Conductance and conductivity are the additive properties, e.g. if an aqueous solution contains more than one electrolyte the total conductance is

en by 
$$G_T = \sum_{i=1}^{n} G_i + G_{water}$$

aive

Conductance of all ions

**③** TRANSPORT NUMBER

It is defined as the fraction of current carried by an ion in an electrolytic solution.

Transport number =  $\frac{\text{Current carried by an ion}}{\text{Total current carried}}$ 

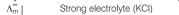
Transport number of cation + Transport number of anion = 1

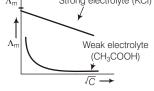
### **KOHLRAUSCH'S LAW** (FOR WEAK ELECTROLYTES)

Whether strong or weak electrolyte, the equivalent conductance increases with dilution and reaches to maximum value at infinite dilution. According to Kohlrausch's law, at infinite dilution  $\Lambda_{\infty} = \lambda_a + \lambda_c$  where,  $\Lambda_{\infty} =$  Equivalent conductance at infinite dilution  $\lambda_a$  and  $\lambda_c$  are ionic conductances of anion and cation at infinite dilution respectively. Degree of dissociation,  $\alpha = \lambda_c / \lambda_{\infty}$ .

#### EFFECT OF ELECTROLYTE

(i) The plot of Λ<sub>m</sub> vs√C for weak and strong electrolytes is shown in figure given below. It is clear from the plot that for a strong electrolyte extrapolation of curve to C = 0 gives Λ<sub>m</sub> for strong electrolytes. However, such an extrapolation cannot be made for weak electrolyte.





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## **ELECTROCHEMICAL SERIES**

In electrochemical series the elements are arranged increasing order of their standard reduction potentials. The table below shows the electrochemical series. Standard Electrode Potential at 25°C

The Electrochemical Series

Element		Electrode reaction (reduction)		elec redu	ndard trode uction al, <i>E</i> ° (vo
Li	1	$Li^+ + e^- \longrightarrow Li$	,	•	-3.05
К		$K^+ \; + e^- \longrightarrow \; K$			-2.925
Na		Na <sup>+</sup> +2e <sup>-</sup> $\longrightarrow$ Na			-2.714
Mg	t	$Mg^{2+} + 2e^- \longrightarrow Mg^{2+}$	g		- 2.37
Al <u>G</u> o	agent	$AI^{3+} + 3e^- \longrightarrow AI$	ent	S	- 1.66
Zn the	ing	$Zn^{2+} + 2e^- \longrightarrow Zn$	agent	tron	- 0.762
Fe	kidis	$Fe^{2+} + 2e^- \longrightarrow Fe$	cing	elec	-0.44
Ni 2 to	as oxidising	$Ni^{2+} + 2e^{-} \longrightarrow Ni$	edur	ose ele oxidati	- 0.25
Sn geno	gth a	$\operatorname{Sn}^{2+} + 2e^{-} \longrightarrow \operatorname{Sn}^{2+}$	as reducing	for lo	-0.14
H <sub>2</sub> tenc	trenç	$2H^+ + 2e^- \longrightarrow H_2$		ency	0.00
B B b S P S P S S P S S S P S S S S P S	ncreasing strength	$Cu^{2+} + 2e^- \longrightarrow Cu$	strength	ncreasing tendency to lose electrons ncreasing tendency for oxidation	+ 0.33
Ag Leas	asir	$Ag^+ + e^- \longrightarrow Ag$		ng te	+ 0.799
Hg <u>L</u> L	ncre	$Hg^{2+} + 2e^- \longrightarrow Hg$	ncreasing	ncreasing ncreasing	+ 0.885
Br <sub>2</sub>	-	$\mathrm{Br}^+_2 + 2e^- \longrightarrow 2\mathrm{Br}^-$	ncré	ncre	+1.08
CI <sub>2</sub>		$\mathrm{Cl}_2^+ + 2\mathrm{e}^- \longrightarrow 2\mathrm{Cl}^-$			+1.36
Au		$\mathrm{Au}^{3+} + 3\mathrm{e}^- \longrightarrow \mathrm{Au}$			+1.50
F <sub>2</sub>	ł	$F_2^+ + 2e^- \longrightarrow 2F^-$			+2.87

- (ii) For weak electrolytes, conductivity increases steeply but Λ<sub>m</sub><sup>∞</sup> cannot be obtained at zero concentration because at such a concentration, the conductivity of solution is so low that it cannot be measured accurately. Thus, for weak electrolytes, Λ<sub>m</sub><sup>∞</sup> is obtained by Kohlrausch's law of independent migration of ions.
- (iii) The equivalent and molar conductivities at infinite dilution are denoted by  $\Lambda^{\infty}$  and  $\Lambda^{\infty}_{m}$  respectively. The variation of molar conductances for strong electrolyte with concentration is given by Debye-Huckel Onsager equation which is  $\Lambda_{m} = \Lambda^{\infty}_{m} b\sqrt{C}$

where, b = constant, C = concentration,

 $\Lambda_{\rm m}^{\infty}$  = molar conductance at infinity.

## EFFECT OF TEMPERATURE OVER CONDUCTIVITY

The conductance of an electrolyte increases with increase in temperature of solution. It is due to the reason that on increasing the temperature of the solution, the kinetic energy of ions increases resulting increase in the movement of ions. Over a small range of temperature, the

# PT MAP ision Tool HEMISTRY

#### CHARACTERISTICS

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t)

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- (i) Elements having negative SRP when joined to SHE behave as anode and those having positive SRP when joined to SHE behave as cathode.
- (ii) Elements which are better reducing agent than hydrogen are placed above hydrogen and the elements which are better oxidising agent than hydrogen placed below hydrogen in this series.

#### APPLICATIONS

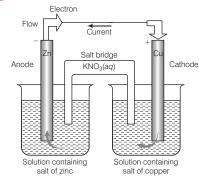
- (i) Metal with lower SRP value displaces metal with higher SRP from its solution. Hence, reactivity of metals decreases from top to bottom in electrochemical series.
- (ii) Elements above hydrogen displace hydrogen in any protic solution, whereas elements below hydrogen are unable to displace hydrogen.
- (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 extraction of metal Less electropositive metals are displaced from their ores by adding salts of more electropositive metal.
- (vi) Predicting product of electrolysis, when more than one type of positive or negative ions are present, the stronger oxidising agent out of the given cations and the reducing agent among the given anions that are liberated at cathode and anode.

temperature dependence of molar conductivity is given by the equation of the type.

$$\Lambda_{\rm m} = \Lambda_{\rm m\,(25)}[1 + \beta(t - 2b)]$$

where,  $\beta = \text{constant}$ ,  $\Lambda_m = \text{conductivity}$  at t °C. Molar conductivity in dilute solutions near room temperature changes by about 2% per degree change in temperature.

## **5** ELECTROCHEMICAL CELL



• It is also called as galvanic cell or voltaic cell.

- It is used to produce electricity by chemical change.
- In this cell ions are discharged only at cathode.
- Besides salt bridge in this cell, both the electrodes are connected externally with the help of a wire connected through a voltmeter.

#### TYPES OF VOLTAIC CELL

- (i) Primary voltaic cell In this cell, current cannot be regenerated by reversing current flow by external circuit chemicals, once consumed, the further reaction is not possible. e.g. dry cell.
- (ii) Secondary voltaic cell In this cell, the original reactants can be regenerated by passing direct current from external source. e.g. lead storage battery.

#### REPRESENTATION OF VOLTAIC CELL

Anode (oxidation half-cell) | Salt bridge | cathode (Reduction half-cell)

 $Zn|Zn^{2+}||Cu^{2+}|Cu$ 

#### **6** ELECTRODE POTENTIAL

It is the quantity which measures the tendency of an electrode to gain or lose electrons in the half-cell. It further can be classified into two types

#### (I) OXIDATION POTENTIAL $(E_{oxi})$

The tendency of an electrode to lose electron or to get oxidised.

e.g.  $M(s) = M^{n+}(aq) + ne^{-}$ 

#### (II) REDUCTION POTENTIAL ( $E_{red}$ )

The tendency of an electrode to gain electrons or to get reduced.

e.g.  $M^{n+} + n\overline{e} \iff M(s)$ 

Note  $E_{\text{oxi}} = -E_{\text{red}}$ , the half-cell reactions are always written as reduction half-cell reactions and their potentials are represented as reduction potentials.

### **7** STANDARD ELECTRODE POTENTIAL $(E^{\circ})$

- (i) It is equal to the electrode potential when concentration of electrolytic solution is taken 1 M and temperature is 298 K.
- (ii) If the electrode involves in gas phase, the standard conditions are choosen as : 1 atm pressure and 1 M concentration of electrolyte at 298 K.

## **8** EMF OF A GALVANIC CELL

The difference in electrode potentials of electrodes is called electromotive force (emf) or cell potential of cell

 $emf = E_{red}$  (cathode) –  $E_{red}$  (anode)

or  $emf = E_{oxi}$  (anode) +  $E_{red}$  (cathode)

#### **9** NERNST EQUATION

It relates the electrode potential of an electrochemical cell to the concentrations of reactants and products of a chemical reaction, at any point of time.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

#### APPLICATIONS OF NERNST EQUATION

(i) In the calculation of potential of a concentration cell. For a concentration cell,  $M / M^{2+}$  (conc.)|| $M^{2+}$  (dil.)|M

$$E_{\text{cell}} = -\frac{2.303RT}{nF} \log \frac{[M^{2+}]_{\text{LHS}}}{[M^{2+}]_{\text{RHS}}}$$

(ii) In the measurement of pH of concentration cell,

$$pH_{unknown} = \frac{E_{cell}}{0.0592}; [H^+]_{known} = 1 M$$

(iii) In the measurement of equilibrium constant of an electrochemical reaction,  $E_{cell}^{\circ} = \frac{2.303 RT}{nF} \log K_C$ 

## GIBBS FREE ENERGY @ ELECTRO CHEMISTRY

It is infinite amount of energy which release when all spontaneous processes come from higher energy state to lower energy state.

#### GIBBS FREE ENERGY CHANGE FOR ELECTROCHEMICAL CELLS

 $\Delta G = - nFE_{\text{cell}}$ 

where, F = Faraday's constant n = number of moles of electrons transferred At equilibrium,  $\Delta G^{\circ} = -2.303 RT \log K_{C}$ 

FEASIBILITY OF A CELL REACTION

$$\Delta G^{\circ} = - nFE^{\circ}$$

For the reaction to be feasible,  $\Delta G^{\circ} < 0$  $E^{\circ} > 0$  or  $\Delta G < 0$  and E > 0

## **D** BATTERY OR CELL

It is basically a galvanic cell used where the chemical energy of redox reaction is converted into electrical energy.

#### **TYPES OF BATTERIES**

- (i) Primary batteries These are the batteries in which cell reaction occurs only once and the battery becomes dead after use over a period of time and cannot be reused again, e.g. dry cells like Leclanche cell, mercury cell etc.
- (ii) Secondary batteries These are the batteries which can be recharged by passing current through it in opposite directions, so that it can be used again, e.g. lead storage battery and nickel cadmium battery.

#### **P**FUEL CELLS

In a fuel cell, continuous energy can be obtained, as long as the outside supply of fuel is maintained, fuel cells are efficient and pollution free e.g. hydrogen-oxygen

Anode  $[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$ 

Cathode  $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-$ 

**Overall**  $2H_2(g) + O(g) \longrightarrow 2H_2O(l) + Heat$ 

## B CORROSION

The gradual destruction of a metal by oxidants present in the surrounding of metal is called corrosion. It is an electrochemical process in which the oxidant oxidises the metal into metal oxide. In corrosion of iron (rusting), iron is oxidised to iron oxide in the presence of water and oxygen. The following reaction occur during rusting of iron.

$$\operatorname{Fe}(s) + \operatorname{3O}_2(g) + \underset{\operatorname{From}}{xH_2O} \longrightarrow \operatorname{Fe}_2O_3 \cdot xH_2O$$

The half-cell reaction are Oxidation half-cell  $Fe(s) \longrightarrow Fe^{2+} + 2e^{-1}$ 

Reduction half-cell

 $O_2(g) + 2H_2O + 4e^- \longrightarrow Fe_2O_3 + 4H^+$ 

The formed ferrous ion again reacts with moisture to give ferric oxide.

$$2\mathrm{Fe}^{2^+} + 2\mathrm{H}_2\mathrm{O} + \frac{1}{2}\mathrm{O}_2 \longrightarrow \mathrm{Fe}_2\mathrm{O}_3 + 4\mathrm{H}^+$$

Rusting is a wasting process and can be prevented by galvanisation of iron, by alloying, by electroplating coating of over iron etc.



# POLARITY AND UNSATURATION

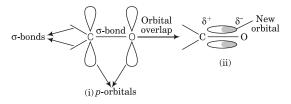
## KEY PLAYERS OF CARBONYL COMPOUNDS BEHAVIOUR

## Coverage of Special Topics for JEE Advanced

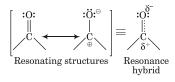
Aldehydes and ketones have general formula *R*CHO and *RR*'CO, respectively where the groups *R* and *R*' *can be aliphatic or aromatic.* Both aldehydes and ketones contain the carbonyl group, >C = 0 and are referred collectively as **carbonyl compounds**.

## Polarity and Unsaturation in Carbonyl Compounds

- Carbonyl compounds give **addition reactions** which shows that these compounds are **unsaturated in nature**.
- In carbonyl compounds, carbonyl carbon is joined to three other species by three  $\sigma$ -bonds. Thus, it is  $sp^2$ -hybridised and attached to oxygen along with other two species directly. These three species attached to the carbonyl carbon lie in a plane and are 120° apart.
- The remaining *p*-orbital of the carbon overlaps with a *p*-orbital of oxygen and forms a  $\pi$ -bond. Thus, carbon and oxygen are joined by a double bond. The orbital picture is given below.



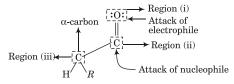
• The difference in electronic distribution on carbon and oxygen atoms in figure (ii) is due to large difference in their electronegativities (electronegativities of carbon and oxygen are 2.5 and 3.5, respectively on pauling scale). As a result, the carbonyl group is best described as a resonance hybrid of the following resonance structures.



### Regions of Reactivity and Types of Reactions Given by Carbonyl Compounds

Aldehydes and ketones contain three regions at which most reactions take place.

- (i) The Lewis basic oxygen
- (ii) The electrophilic carbonyl carbon
- (iii) The adjacent  $\alpha$ -carbon

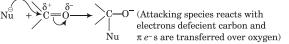


Carbonyl compounds give following types of reaction due to the presence of polar carbonyl group

- (i) Nucleophilic addition reactions
- (ii) Oxidation
- (iii) Reduction
- (iv) Reactions due to  $\alpha$ -hydrogen

## **Polarity** versus Nucleophilic Attack

- The complete transfer of the shared pair of  $\pi$ -electrons of a multiple bond to one of the atoms in the presence of the attacking species is called **electromeric effect**.
- Due to polarity in >C=O bond, in the presence of some reagent (nucleophile), the  $\pi$ -electron pair of carbonyl group is transferred to oxygen.
- As the result, nucleophile attaches itself to the electron deficient carbon of carbonyl group.
- This effect is a temporary effect and takes place only in the presence of the attacking agent.

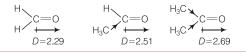


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## METICULOUS ANALYSIS

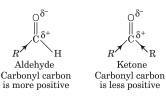
## Polar character versus dipole moment

- Due to greater electronegativity of oxygen, the carbonyl compounds are polar, and have larger molecular dipole moments (D). The resonance structures of carbonyl compounds illustrate this polarity.
- The dipole moment is directly proportional to polar character, i.e. the larger the polar character, the greater is the dipole moment of the carbonyl group.
- The relative dipole moments of formaldehyde and other aldehydes and ketones confirm the stabilising influence that alkyl substituents have on carbocations.



### **Relative Reactivity @ Nucleophilic Addition**

- Generally, aldehydes are more reactive than ketones in nucleophilic addition reactions, as both steric and electronic factors favour aldehydes.
- The central carbon of the tetrahedral product formed from an aldehyde is less crowded and the product is more stable. It is due to small hydrogen atom attached to central carbon atom.
- The central carbon of the tetrahedral product formed from a ketone is more crowded and the product is less stable. It is due to two alkyl substituents at the carbonyl carbon of ketone cause greater steric crowding in the tetrahedral product.
- On the other hand, aldehydes have one electron donating alkyl group while ketones have two electron donating alkyl groups. These alkyl groups stabilise the partial positive charge on carbonyl carbon. **Thus, ketones are more stabilised and less reactive than aldehydes**.



- Note 1. In carbonyl compounds, the presence of oxygen atom with two lone pairs of electrons makes aldehydes and ketones proton acceptors.
  - Electron withdrawing groups

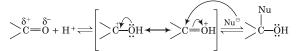
     (e.g. —CF<sub>3</sub> or —CCI<sub>3</sub>, etc.) cause the carbonyl carbon to be more positive and nucleophilic addition reaction to be more favourable.

## Pathways of Mechanism Followed by the Nucleophilic Addition Reactions of Carbonyl Group

Nucleophilic Addition followed by Protonation (Basic Conditions) Outline of mechanism

- This pathway begins with attack of nucleophile under neutral or basic conditions.
- As the nucleophile approaches the electrophilic carbon, the carbon rehybridises and the electron pair of the  $\pi$ -bond moves over to the oxygen, thereby producing an alkoxide ion.
- Subsequent protonation, usually form a protic solvent such as water or alcohol, yields the final product.
- Addition of strongly basic nucleophiles to carbonyl groups typically follow the nucleophilic addition protonation pathway.

#### Protonation followed by Nucleophilic Addition (Acidic Conditions)



- This pathway begins with the attack of reagent's  $\pi$ -electrons to the electrophile (H<sup>+</sup>) and protonation of carbonyl group's oxygen occurs. The oxygen is weakly basic. However, the small amount of protonated material behave like a very reactive carbon electrophile.
- Nucleophilic attack by the nucleophile completes the addition process and shifts the first, unfavourable equilibrium.

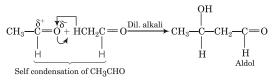
Now let us discuss some important reactions in this article from exam point of view.

## **Condensation Reactions**

These are reactions in which two or more (identical or different) molecules unite with each other with the elimination of simple molecule (like  $\rm H_2O$ ).

#### **Aldol Condensation**

• Aldehyde, in the presence of dilute sodium hydroxide, potassium carbonate or hydrochloric acid, undergoes condensation to form a syrupy liquid known as **aldol**.



- On heating, aldol eliminate water to form  $\alpha$  ,  $\beta$  -unsaturated compounds.

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• When the condensation process occurs between two different carbonyl compounds, then the process is called cross-aldol condensation.

e.g. 
$$CH_3 \rightarrow C = 0 + H \xrightarrow{C} C = 0 \xrightarrow{\bar{O}H} H \xrightarrow{CH_2OH} CH_2CHO$$

- Note The aldol condensation can occur between the following molecules.
  - (i) Two aldehydes (identical or different)
  - (ii) Two ketones (identical or different)
  - (iii) An aldehyde and a ketone

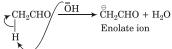
In short, whatever the nature of the carbonyl compound, it is only the  $\alpha$ -hydrogen atoms which are involved in the aldol condensation.

- Enolisation property (ability to convert into enol form on tautomerisation) is responsible for this reaction.
- As tautomerisation (keto-enol) is possible with acid or base both, that is why this reaction can occur in the presence of acid as well as in dilute base.

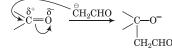
## Mechanism

The mechanism of aldol condensation is summarised as

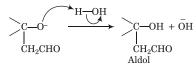
- (i) Nucleophilic addition followed by Protonation (Basic Conditions)
- Step 1 Abstraction of proton from aldehyde or ketone in the presence of alkali



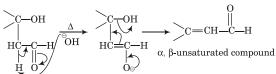
Step 2 Attack of enolate ion on the other carbonyl carbon



**Step 3** Protonation of anion formed in step-2 by H<sub>2</sub>O produced in step-1



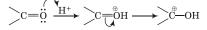
Step 4 On heating, dehydration occurs due to the presence of  $\alpha$ -H.



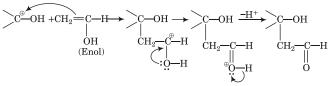
## (ii) Protonation followed by Nucleophilic

Addition (Acidic Conditions)

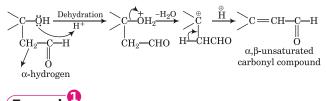
 $Step \ 1$  Protonation of carbonyl group to form carbocation.



Step 2 Attack of  $\pi$ -electrons of double bond of enolic form of aldehyde to the carbocation.



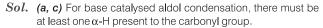
**Step 3** Dehydration due to the presence of  $\alpha$ -hydrogen.

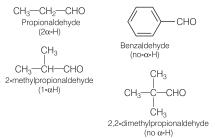


**Example** Base catalysed aldol condensation occurs with

[**IIT 2008**]

- (a) propionaldehyde
- *(b)* benzaldehyde
- (c) 2-methyl propionaldehyde
- (d) 2, 2-dimethylpropionaldehyde

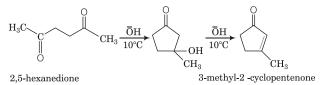




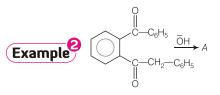
Thus, options (a) and (c) are correct.

## Intramolecular Aldol Condensation

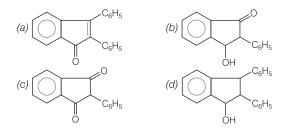
 Aldol condensation proceeds with excellent yield when both carbonyl groups are parts of the same molecule.
 e.g. 2, 5-hexanedione with base leads to the formation of cyclic α, β-unsaturated ketone.



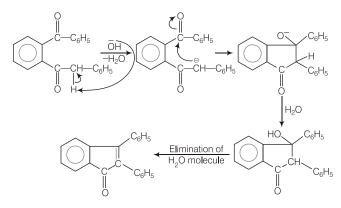
- The dehydration that introduces a double bond into a five member ring is often considerably faster than the analogous reactions resulting in a cyclohexane product.
- Note The aldol condensation of 2, 5-hexanedione (or higher diones) could have produced a product with a four member (or three member) ring. However, because of ring strain, four member (or three member) ring is not observed.



What is the structure of A?



*Sol.* (a) This is an example of intramolecular aldol condensation reaction, the mechanism is given as

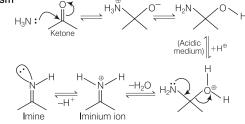


## Nucleophilic Addition of Ammonia and its Derivatives

Ammonia and its derivatives have an unshared electron pair on nitrogen atom and these act as nucleophiles towards the carbonyl carbon atoms.

The reaction of ammonia or a 1° amine with an aldehyde or a ketone forms an **imine**, also known as a **Schiff base**. The reaction of ammonia with an aldehyde or a ketone begins with nucleophilic attack on the carbonyl carbon. However, the higher nucleophilicity of ammonia makes it unnecessary to employ either acid or base catalysis to initiate the reaction.





## NETICULOUS ANALYSIS

The given reaction mechanism can be understood by the following points.

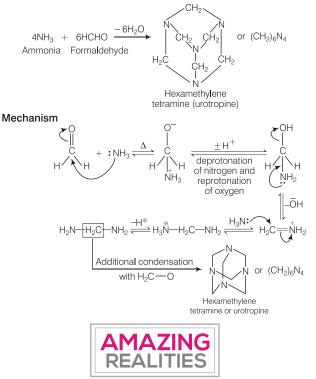
- The lone pair of nitrogen attacks at the carbonyl carbon to generate a tetrahedral Zwitter ionic intermediate. Rapid deprotonation of nitrogen and protonation at oxygen lead to a neutral species.
- But because the intermediate is in protic medium, it can be protonated again, on either oxygen or nitrogen.
- Protonation on nitrogen gives the revert product but protonation on oxygen sets the stage for the loss of water and formation of a C == N bond using nitrogen's lone pair. The resulting iminium ion loses a proton to form a neutral imine.

## REMEMBER

Imines of aldehydes and those derived from ammonia are unstable. These cannot be easily isolated. These are readily converted into the starting ketones and amines in the presence of water.

#### **Mechanism for the Formation of Urotropine**

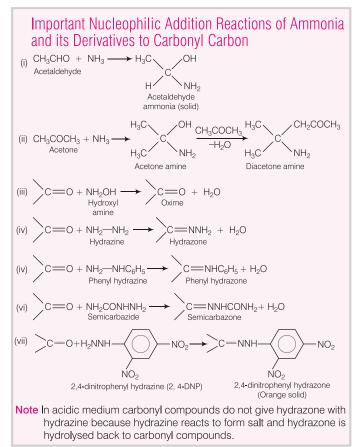
In this reaction ammonia (4 moles) and formaldehyde (6 moles) reacts with each other and give a nucleophilic addition product (Urotropine).



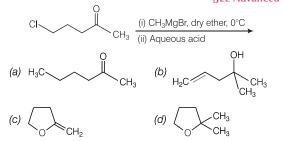
It was only in the 1800s that chemists discovered how to make coloured firecrackers. They identified certain compounds that when used burned to give reds, greens, blues and purples. In the olden days it used to be difficult to produce the colour blue. But with the discovery of magnesium-aluminium alloy - Magnalium, this is no longer a problem.

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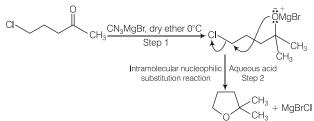


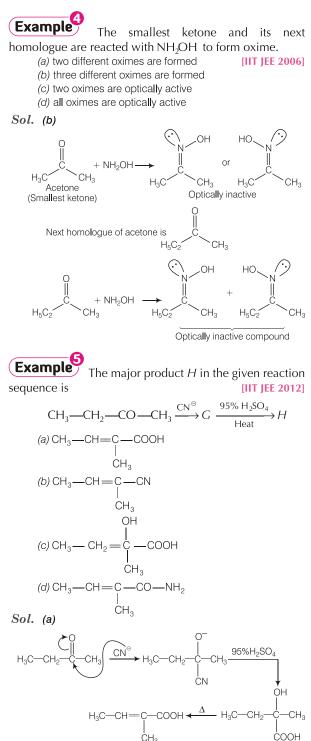
Example The major product in the following reaction is [JEE Advanced 2014]



Sol. (d) Thinking process

- In this problem both nucleophilic addition as well as nucleophilic substitution reactions take place.
- . Nucleophilic addition occurs in step 1 and nucleophilic substitution occurs in step 2.

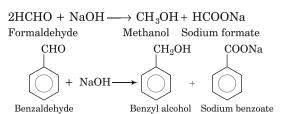




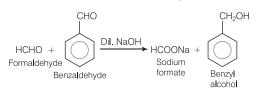
## **Cannizzaro Reaction**

Aldehydes that do not have any  $\alpha$ -hydrogen undergo the Cannizzaro reaction. It is a disproportionation (self oxidation-reduction) reaction in salts of acids in which half of the molecules of aldehyde are oxidised into acids and other half are reduced into alcohols, e.g.

CH



• The Cannizzaro reaction can take place between two different aldehydes and then it is known as **Crossed Cannizzaro reaction**, e.g.



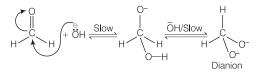
Note Although the Cannizzaro reaction is characteristic of aldehydes which do not have  $\alpha$ -hydrogen atoms, it is not confined to them, e.g. certain aliphatic  $\alpha$ -monoalkylated aldehydes undergo quantitative disproportionation when heated with aqueous sodium hydroxide at 170 – 200°C.

2 (CH<sub>3</sub>)<sub>2</sub>CHCHO + NaOH  $\xrightarrow{200^{\circ}C}$  (CH<sub>3</sub>)<sub>2</sub>CHCOONa

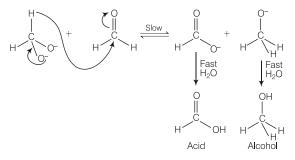
## Mechanism

The mechanism involves the following two steps

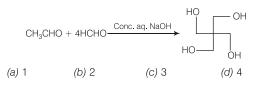
**Step 1** Nucleophilic attack



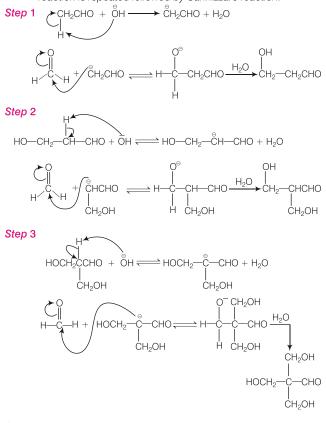
#### Step 2 Hydride ion transfer

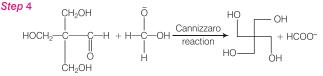


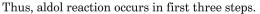
**Example** The number of aldol reactions that occur in the given transformation is [JEE Advanced 2012]

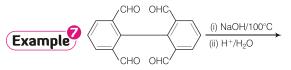


*Sol.* (c) Thinking process In this reaction, aldol condensation reaction is repeated followed by Cannizzaro reaction.



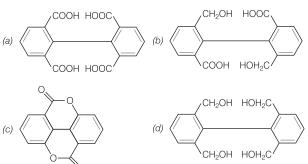






major product is

[IIT JEE 2008]

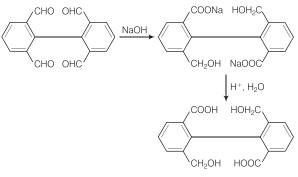


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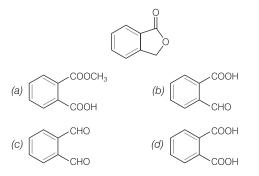
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Sol. (b) Short trick There is no  $\alpha$ -hydrogen present in this molecule. Thus, it will give intramolecular Cannizzaro reaction.

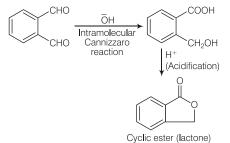


**Example** Which of the following reactants on reaction with conc. NaOH followed by the acidification gives following lactone as the main product? [IIT JEE 2006]

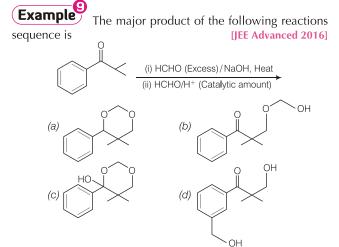


#### Sol. (c) Thinking process

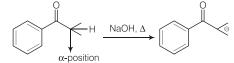
- The given product is a cyclic ester.
- We know that, ester is formed by the reaction between alcohol and acid followed by acidification.
- So, we have to decide which compound among the given compounds will contain both acid (-COOH) and alcohol -OH) groups after reaction with conc. NaOH.
- Now, as we know that in Cannizzaro reaction, reactant(s) give both acid and alcohol on reaction with conc. NaOH. So, the compound should not contain  $\alpha$ -hydrogen in order to give Cannizzaro reaction.
- The compound in option (c), does not contain any  $\alpha$ -hydrogen so, it will give the desired product.



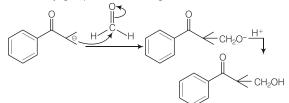
Thus, the compound mentioned in option (c), will give lactone followed by intramolecular Cannizzaro reaction and acidification.



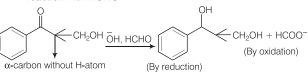
- Sol. (a) You can solve this problem by going through the following steps
- Step 1 As alkali is a base, so it abstracts proton from a-position of carbonyl group and generates carbanion.



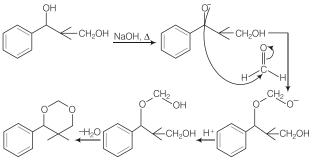
Step 2 This carbanion further attacks at electron deficient carbon of carbonyl group of HCHO and gives crossed-aldol reaction.



Step 3 Now the product obtained from crossed-aldol reaction, does not have any α-hydrogen. Thus, it further gives Cannizzaro reaction with HCHO.



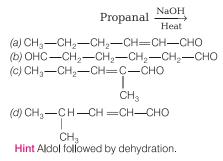
Step 4 In the final step, alkali abstracts proton from the 2°-alcohol, as electron withdrawing benzene ring is attached to it and further it reacts with HCHO to form acetal.



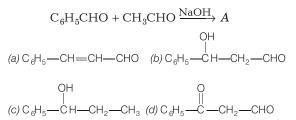
# Smart Practice

## **Single Answer Correct Type**

**1.** What is the product of the following reaction?

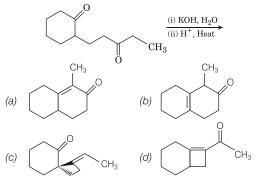


**2.** Complete the following reaction and find the structure of product(*A*).

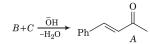


Hint Crossed-aldol condensation.

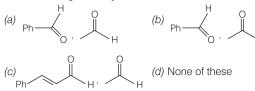
**3.** The major product of the following reaction is



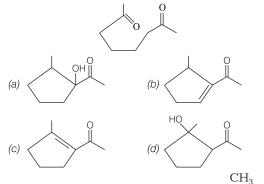
**4.** Compound (A) is formed by the aldol reaction between B and C.



#### B and C respectively are



5. The compound given below undergoes intramolecular aldol condensation reaction, when heated in alkali to give

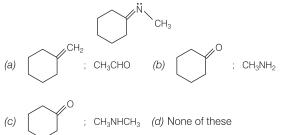


**6.**  $C_3H_6O \xrightarrow{\bar{O}H} A \xrightarrow{NaHSO_4} CH_3CH_2CH = CCHO$ 

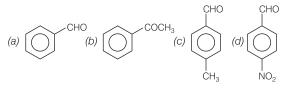
The compound C<sub>3</sub>H<sub>6</sub>O is

(a)  $CH_3COCH_3$  (b)  $CH_3CH_2CHO$ (c)  $CH_2 = CHCH_2OH$  (d)  $CH_3 - C = CH_2$ |OH

7. The following imine can be prepared by



**8.** Which one is the most reactive towards nucleophilic addition reaction?



Hint Electron withdrawing group at *ortho* or *para* position in benzaldehyde, facilates nucleophilic addition reaction.

- **9.** Which of the following will not undergo aldol condensation?
  - (a) Acetaldehyde
  - (b) Propionaldehyde
  - (c) Trideutereo acetaldehyde
  - (d) Benzaldehyde

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**10.** In the following Cannizzaro reaction, which is the slowest step?

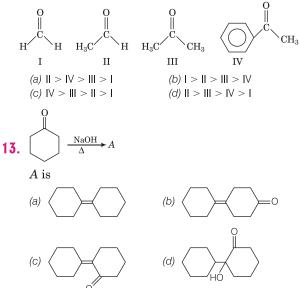
## $2 PhCHO \xrightarrow{\bar{O}H} PhCH_2OH + PhCOO^-$

- (a) The attack of  $\overline{O}H$  at the carbonyl group
- (b) The transfer of hydride to the carbonyl group
- (c) The abstraction of proton from the carboxylic acid
- (d) The deprotonation of PhCH<sub>2</sub>OH
- Among the following compounds, the one which can undergo both aldol condensation and Cannizzaro reaction is

   (a) (CH<sub>3</sub>)<sub>2</sub>CHCHO
   (b) HCHO

(a) (CH <sub>3</sub> ) <sub>2</sub> CHCHO	(b) HCHO
(c) C <sub>6</sub> H <sub>5</sub> CHO	<i>(d)</i> CH <sub>3</sub> CHO

**12.** Arrange the following compounds in the decreasing order of nucleophilic addition reaction.



**14.** Acetaldehyde reacts most readily with (a)  $H_2N$ — $NH_2$  (b)  $H_2N$ —NH—C—

(c) Ph—NH—NH<sub>2</sub>

(b)  $H_2N$ —NH—C— $NH_2$  $\parallel$ (d)  $H_2N$ —OH

## More than One Correct Type

**15.** Among the following compounds, which will react with acetone to give a product containing

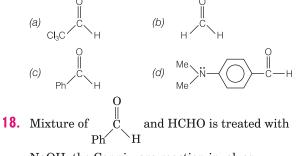
 $\begin{array}{c} & \searrow C = N - \\ (a) \ C_{6}H_{5}NH_{2} & (b) \ (CH_{3})_{3}N \\ (c) \ C_{6}H_{5}NHC_{6}H_{5} & (d) \ C_{6}H_{5}NHNH_{2} \end{array}$ 

**16.** Cannizzaro reaction will be given by



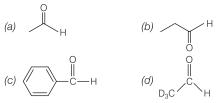
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**17.** Which of the following do not give Cannizzaro reaction?

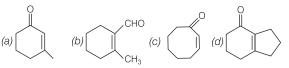


NaOH, the Cannizzaro reaction involves(a) Reduction of HCHO(b) Oxidation of HCHO(c) Reduction of PhCHO(d) Oxidation of PhCHO

**19.** Which of the following will undergo aldol condensation?



**20.** Which of the following compounds can be synthesised by intramolecular aldol condensation in very good yield?



**21.** Which of the statements are correct about the internal or intramolecular Cannizzaro reaction given below?

(a) ŌH attacks at carbon-1

- (b)  $\overline{O}$  H attacks at carbon-2
- (c)  $H^-$  transfer takes place from C-1 to C-2
- (d) H<sup>+</sup> exchanges from acid to alkoxide
- **22.** During the reaction between carbonyl compounds with ammonia derivatives, a proper pH is required. Select the correct reasons.
  - (a) To increase positive charge on the carbon atom of carbonyl group for the better attack of nucleophilic centre of ammonia derivative, a small amount of acid is needed
  - (b) With excess of acid, ammonia derivatives form their salts and act as strong nucleophiles
  - (c) With excess of acid, ammonia derivatives form their salts and cannot act as nucleophiles
  - (d) The proper pH required for these reactions is nearly 3 to 5

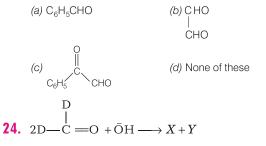
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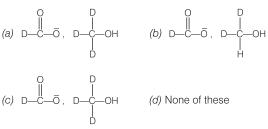
#### Passage-I

Aldehydes which do not contain  $\alpha$ -hydrogen atom, when treated with concentrated alkali, undergo self oxidationreduction to yield a mixture of an alcohol and a salt of carboxylic acid. This reaction is known as Cannizzaro reaction and it is carried out at room temperature.

**23.** Which of the following can't undergo Cannizzaro reaction?



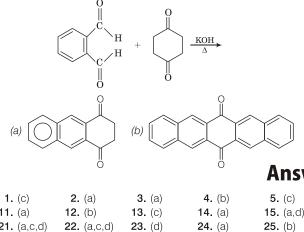
X and Y will have structures

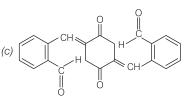


## Passage-11

The addition reaction of enol or enolate to the carbonyl group of aldehyde or ketone is known as aldol addition. The  $\beta$ -hydroxyaldehyde or  $\beta$ -hydroxyketone so obtained undergo dehydration in second step to produce a conjugated enone. The first part of reaction is an addition reaction and the second part is an elimination reaction.

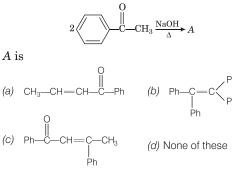
**25.** Find out the major product of the following reaction.





(d) None of the above

**26.** The product of the following reaction is



#### Passage-III

When acetone was allowed to react with semicarbazide O

 $(H_2N - NH - C - NH_2)$ , semicarbazone was formed. In its formation out of the three nitrogen atoms of semicarbazide, only one nitrogen atom acted as a nucleophile and attacked the carbonyl group of acetone.

**27.** Which one was the chemical formula of acetone semicarbazone?

(c) Both (a) and (b) (d) None of these28. Semicarbazone is a/an

(b)  $(CH_3)_2 C = NNHCONH_2$ 

(a) condensation product(b) addition product(c) elimination product(d) substitution product

#### **Integer Type**

**29.** In the following reaction, the total number of intramolecular aldol condensation products formed is/are



**30.** How many nitrogen atoms are present in the structural formula of the main organic product formed when methanal reacts with ammonia?

## Answers

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

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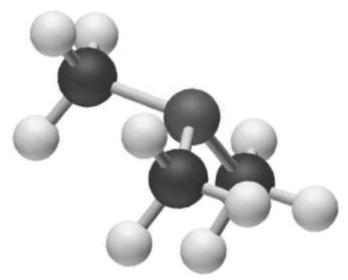
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# NOMENCLATURE OF ORGANIC COMPOUNDS PART 4



This section is targetted to provide an insight of IUPAC nomenclature of organic and inorganic compounds through questions as every year atleast 1-2 questions are asked on IUPAC nomenclature in all the competitive exams and boards.

## **Naming of Aliphatic Hydrocarbons**

• We have read about branch selection and numbering in cyclic and aromatic compounds in the last issue. Now, we are going to learn groupwise nomenclature through examples from this issue. Before steping forward, lets rememberise the formula which we discussed in June 2016 issue.

 $2^{\circ}$ -prefix +  $1^{\circ}$ -prefix + Word root +  $1^{\circ}$ -suffix +  $2^{\circ}$ -suffix

• In this issue we shall learn mainly nomenclature of hydrocarbons. For various hydrocarbons, use the word roots given below :

Chain length	Word root	Chain length	Word root
$C_1$	Meth-	$C_7$	Hept(a)-
$\mathrm{C}_2$	Eth-	$C_8$	Oct(a)-
$C_3$	Prop(a)-	C <sub>9</sub>	Non(a)-
$C_4$	But(a)-	$C_{10}$	Dec(a)-
$C_5$	Pent(a)-	C <sub>11</sub>	Undec(a)-
$C_6$	Hex(a)-	$C_{12}$	Dodec(a)-

• For naming of side chains or 2°-prefix use the following formula

 $\begin{aligned} Alkane - ane + yl &= Alkyl\\ Alkene - e + yl &= Alkenyl\\ Alkyne - e + yl &= Alkynyl \end{aligned}$ 

Example CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

Sol. Rule Remove 'a' from word root if first letter of 1°-suffix is a vowel.

Common name *n*-hexane IUPAC name Hexa + ane = Hexane ↓ ↓ Word root 1°-suffix

 Image: Constraint of the second se

2 -methyl + buta + ane = 2 -methylbutane  $\downarrow$   $\downarrow$   $\downarrow$   $\downarrow$ 1°-prefix Word root 1°-suffix

$$\begin{array}{c} \textbf{Example}^{\textcircled{\textbf{S}}} \\ \textbf{CH}_3 - \textbf{CH}_4 - \textbf{CH}_2 - \textbf{CH}_3 \\ \begin{matrix} I \\ CH_3 \\ CH_3 \end{matrix}$$

**Sol.** Rule When two or more side chains are present on the principal chain, these are prefixed in alphabetical order.

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## **IUPAC IDOLISER**

3-ethyl-2-methylpentane 2-methyl-3-ethylpentane

(

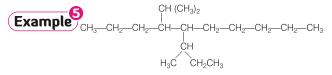
© ① CH<sub>2</sub>—CH<sub>3</sub> 3] ④ Sol. CH<sub>3</sub>—CH—CH—CH<sub>2</sub>—CH ⑤| ⑥ ⑦ CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

(

4-ethyl-3-methylheptane 3-methyl-4-ethylheptane (Correct) (Incorrect)

(Correct)

(Incorrect)



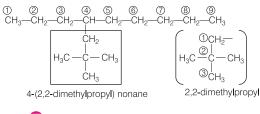
**Sol.** Rule The prefixes cyclo, iso and neo are considered in alphabetically substituted groups while tert and sec are not considered in alphabetically groups.

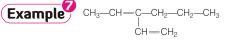
$$\begin{array}{c} CH (CH_3)_2 \\ (CH_3)_2 CH_2 - CH_3 \\ CH \\ H_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \end{array}$$

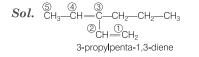
5-sec-butyl-4-iso-propyldecane

Example 
$$CH_3$$
— $CH_2$ — $CH_3$   
 $H_3C$ — $C$ — $CH_3$   
 $CH_3$ 

**Sol.** In case of complex substituent on the principal chain, it is named as substituted alkyl group and numbering in complex substituent is done according to the numbering rules. The name of the complex chain is written in brackets to avoid confusion with the number of main chain.





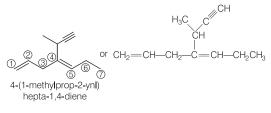


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## **Example** $CH_3 - CH = CH - CH_2 - CH_2 - C \equiv CH$

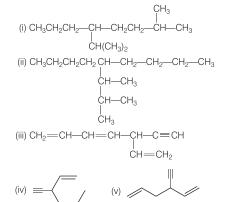
**Sol.** Rule If two 1°-suffixes with unsaturation are present in the principal chain.

**Sol.** Rule If there is a choice between double bond and triple bond during the selection of longest carbon chain, double bond is preferred over triple bond.

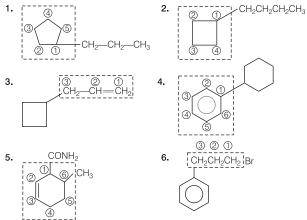


## **Practice Problems**

Write the IUPAC names of the following compounds.



## Practice Problems Answer (August 2016) Issue



## 🔁 RAINBOW

# Learn Through Problems GASEOUS STATE

Gaseous state is an important topic of chemistry. Every year one or two problems is/are asked in medical or engineering entrance exams. This section is targetted to provide stepwise learning and practice through selective problems

*.*..

STEP

- $\square$  A mixture of ethane (C<sub>2</sub>H<sub>6</sub>) and ethene (C<sub>2</sub>H<sub>4</sub>) occupies 40 L at 1 atm and 400K. The mixture reacts completely with 130 g of  $O_2$  to produce  $CO_2$ and H<sub>2</sub>O. Assuming ideal gas behaviour, calculate the mole fractions of  $C_2H_4$  and  $C_2H_6$  in the mixture.
  - STEP-1 Write down the ideal gas equation and calculate the total moles of gaseous mixture.

$$pV = nRT$$
  $\therefore$   $n = \frac{pV}{RT} = \frac{1 \times 40}{0.082 \times 400} = 1.22$ 

STEP-2 Write the balanced combustion reaction of ethane and ethene.

 $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O; C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$ 

STEP-3 Calculate the total moles of O<sub>2</sub> required by considering that mixture contains x moles of ethane.

Moles of ethene = 1.22 - x

Total moles of O<sub>2</sub> required  $=\frac{7}{2}x + 3(122 - x) = \frac{x}{2} + 3.66$ 

Given moles of  $O_2 = \frac{130}{22}$ 

Thus,

$$\frac{130}{32} = \frac{x}{2} + 3.66$$
$$x = 0.805 \text{ mol}$$

Moles of ethene = 1.22 - x = 0.415 mol

STEP-4 Write the formula of mole fraction and calculate the mole fraction of ethane and ethene.

Mole fraction of ethane =  $\frac{1}{\text{Total moles of mixture}}$  -0.805= 0.661.22Mole fraction of ethene = 1 - 0.66 = 0.34

## **Try These!**

**1.** Equal weights of methane and oxygen are mixed in an empty container at 25°C. Calculate the fraction of the total pressure exerted by oxygen.

(d) 1/ 3 (D) 1/ 4 (C) 1/2 (d) 1	(a) 1 / 3	(b) 1 / 4	(c) 1/2	(d) 1/5
---------------------------------	-----------	-----------	---------	---------

2. An LPG cylinder, containing 15 kg butane at 27°C and 10 atm pressure is leaking. After one day, its pressure decreases to 8 atm. Calculate the quantity of gas leaked.

(a) 2 kg				(b) 3 kg
(c) 4 kg				(d) 5kg

5.5 mg of nitrogen gas dissolves in 180 g of water at 273 K and 1 atm pressure due to nitrogen gas. Calculate the mole fraction of nit of nitrogen.

nitrogen in T	80 g ot '	water at 5	atm pressure
(a) $1 \times 10^{-3}$			(b) $2 \times 10^{-3}$
(c) $1 \times 10^{-4}$			(d) $2 \times 10^{-4}$
🕥 1. (a)	<b>2.</b> (b)	<b>3.</b> (c)	

- **2** A gas bulb of 1 L capacity contains  $2 \times 10^{21}$  mole of nitrogen exerting a pressure of  $7.57 \times 10^3$  Nm<sup>-2</sup>. Calculate the root mean square (rms) speed and the temperature of the gas molecules. If the ratio of the most probable speed to root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature.
  - STEP-1 Calculate the number of moles of nitrogen by using the formula

Number of moles 
$$(n) = \frac{N(\text{number of molecules})}{N_A(\text{Avogadro's number})}$$
  
 $\therefore \qquad n = \frac{2 \times 10^{21}}{6 \times 10^{23}} = 0.33 \times 10^{-2}$ 

STEP-2 Calculate the temperature of the gas molecules by writing ideal gas equation.

$$pV = nRT$$
$$T = \frac{pV}{nR} = \frac{7.57 \times 10^3 \times 10^{-3}}{0.33 \times 10^{-2} \times 8.314} = 276 \text{ K}$$

STEP-3 Write the formula of  $U_{\rm rms}$  and substitute all the known values

$$\begin{split} U_{\rm rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 276}{28 \times 10^{-3}}} \,\,{\rm ms^{-1}} = 496 \,\,{\rm ms^{-1}} \\ \text{4-4 Using the ratio of } \frac{U_{\rm mps}}{U_{\rm rms}}, \, \text{calculate the value of } U_{\rm mps} \\ \frac{U_{\rm mps}}{U_{\rm rms}} = 0.82 \end{split}$$

 $U_{\rm mbs} = (0.82 \times 496) \,{\rm ms}^{-1} = 407 \,{\rm ms}^{-1}$ 

## **Try These!**

- 1. The average velocity of an ideal gas molecule at 27°C is 0.3 m/s. Calculate the average velocity at 927°C. [IIT JEE 2006] (a) 0.6ms<sup>-1</sup> (b) 1. 7ms<sup>-1</sup> (c) 1.6 ms<sup>-1</sup> (d) 1.0 ms<sup>-1</sup>
- At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. Calculate the molecular weight of the gas Y.

			[III JEE 2009]
(a) 2	(b) 4	(c) 6	(d) 8
🕥 1. (a)	<b>2.</b> (b)		

- 3 A spherical balloon of 21cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up.
  - STEP-1 Calculate the volume of balloon.

## 🔁 RAINBOW

Volume of balloon

$$=\frac{4}{3}\pi r^{3} = \frac{4}{3} \times 3.14 \times \left(\frac{21}{2}\right)^{3} \text{ cm}$$
$$= 4847 \text{ cm}^{3} = 4.85 \text{ L}$$

**STEP-2** Calculate the volume of  $H_2(g)$  in cylinder when it is converted into NTP volume, using  $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$  $\frac{20 \times 2.82}{300} = \frac{1 \times V_2}{273}$  $V_2 = 51.324 L$ **STEP-3** Calculate the available volume of  $H_2(g)$ Initially cylinder will hold 2.82 L of  $H_2(g)$  when equilibrium with balloon establish,.

Available volume of  $H_2 = 51.324 - 2.82 = 48.504 L$ 

**STEP-4** Calculate the number of balloon that can be filled up Number of balloons =  $\frac{48.504}{1000} = 10$ 

 $\frac{4.85}{4.85} = 10$ 

## **Try These!**

 Calculate the volume occupied by 5 g of acetylene gas at 50°C and 740 mm pressure.

(a) 1.85 L	(b) 4.95 L
(c) 6.28 L	(d) 5.23 L

2. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mole of He and 1.0 mole of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, calculate the total volume (in litre) of the gases at 0°C is close to [IIT JEE 2011]

(a) 4 L
(b) 7 L
(c) 6 L
(d) 5 L

4 An LPG cylinder weighs 14.8 kg when empty. When full it weighs 29 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder reduces to 23.2 kg.

Find out the volume of the gas (in cubic metres) used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to the *n*-butane with normal boiling point of  $0^{\circ}$ C.

STEP-1 Calculate the weight of LPG used by using initial weight (14.8 kg) and final weight of LPG(23.2 kg)

Weight (14.6 kg) and final weight of LFG(25.2 kg) Weight of *n*-butane gas remaining = (23.2 - 14.8) kg = 8.4 kg STEP-2 Calculate the pressure inside the cylinder by using pressure (*p*)  $\propto$  moles (*n*). Since, during use, volume of cylinder (*V*) and temperature (*T*) remains same therefore,

$$\frac{p_1}{p_2} = \frac{n_1}{n_2} = \frac{w_1}{w_2}$$
$$p_2 = \left(\frac{w_2}{w_1}\right) p_1 = \left(\frac{8.4}{14.2}\right) \times 2.5 = 1.47 \text{ atm}$$

STEP-3 Now, using ideal gas equation, calculate the volume of LPG used under normal usage conditions ( $p_{outside}$  of cylinder = 1 atm)

$$pV = nRT$$
$$V = \frac{nRT}{p} = \left(\frac{(14.2 - 8.4) \times 10^3}{58} \times \frac{0.082 \times 300}{1}\right) L$$
$$= 2460 L = 2.46 m^3$$

- 1. Oxygen is present in 1 L flask at a pressure of  $7.6 \times 10^{-10}$  mm of Hg.Calculate the number of oxygen molecules in the flask at 0°C.(a)  $2.6 \times 10^{10}$ (b)  $2.6 \times 10^8$ (c)  $3.8 \times 10^8$ (d)  $3.8 \times 10^{10}$
- **2.** When 2 g of a gas *A* is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atm. If 3 g of another gas *B* is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights of  $M_A: M_B$ . [IIT JEE 2007] (a) 3 : 1 (b) 1 : 3 (c) 1 : 2 (d) 2 : 1 (c) 1. (a) 2. (b)

**5** The average velocity at  $T_1$  K and the most probable velocity at  $T_2$  K of CO<sub>2</sub> gas is  $9 \times 10^4$  cm s<sup>-1</sup>.

Calculate the value of  $T_1$  and  $T_2$ .

(2) **STEP-1** Write down the formula of average velocity  $(u_{av})$  at  $T_1$  K.  $u_{av} = \sqrt{\frac{8RT_1}{2}}$ 

$$u_{\rm av} = \sqrt{\frac{8RI_1}{\pi M}}$$

**STEP-2** Put the values of  $u_{av}$ , R,  $\pi$  and M in the above formula and calculate  $T_1$ .

$$\frac{9 \times 10^4}{100} \text{ ms}^{-1} = \sqrt{\frac{8 \times 8.314 \ T_1}{3.14 \times 44 \times 10^{-3}}}; \ T_1 = 1682.5 \text{ K}$$

**STEP-3** Write down the formula in the form of ratio of  $u_{av}$  to  $u_{mps}$ .

$$\frac{u_{\rm av}}{u_{\rm mps}} = \sqrt{\frac{8RT_1}{\pi M}} : \sqrt{\frac{2RT_2}{M}} = \sqrt{\frac{8T_1}{\pi}} \times \frac{1}{2T_2} = \sqrt{\frac{4T_1}{\pi T_2}}$$

**STEP-4** Substitute the value of  $T_1$  in the above ratio and equate with one (since for the same gas)  $\frac{u_{av}}{u_{av}} = 1$ 

$$1 = \sqrt{\frac{4 \times 1682.5}{3.14 \ T_2}}; \ T_2 = \frac{4 \times 1682.5}{3.14} = 2143 \ \mathrm{K}$$
$$T_1 = 1682.5 \ \mathrm{K}; \ T_2 = 2143 \ \mathrm{K}$$

## **Try These!**

- Calculate the root mean square velocity of ozone (in ms<sup>-1</sup>) kept in a closed vessel at 20°C and 82 cm mercury pressure.
   (a) 390.2
   (b) 490.2
   (c) 350.6
   (d) 472.9
- Calculate the temperatures (in K) at which the root mean square velocity, the average velocity and the most probable velocity of

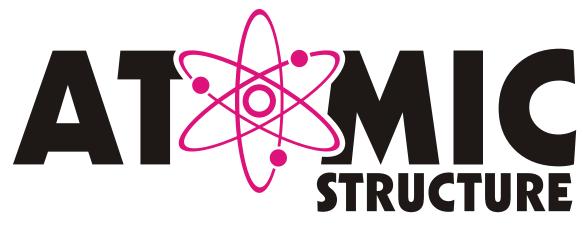
oxygen gas are equal to  $1500 \text{ ms}^{-1}$ .

T <sub>1</sub> (rms) (a) 3399 (b) 4330 (c) 2886	T <sub>2</sub> (av) 4330 3399 3399	T <sub>3</sub> (mp) 2886 2886 4330
(c) 2886	3399	4330
(d) 3399	2886	4330

 Calculate the temperatures (in K) at which the molecules of the first two members of the homologous series C<sub>n</sub>H<sub>2n+2</sub> will have the same rms speed as CO<sub>2</sub> gas has at 770 K.

Τ	for I mem	nber	T for II member
(a)	840		629
(b)	629		840
(c)	525		280
(d)	280		525
<u>ک</u> 1.	(a)	<b>2.</b> (C)	<b>3.</b> (d)



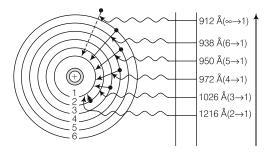


Innovative problems targetted to improve your Conceptual Learning.

- 1. Why is a negative sign used in the formula of Bohr's energy for *n*th orbit?
- O When an electron in the nth orbit is attracted by the nucleus, the energy is emitted and its energy gets lowered. That is why a negative sign is used in the formula of Bohr's energy for *n*th orbit.
- 2. What happens to the atomic levels when a material burns?
- When you give heat to an atom, the electrons move to higher energy orbitals from lower energy orbitals. This phenomenon happens instantaneously. Immediately after this electron moves back down to its lower energy orbital and gives off the excess energy as light that you seen in a fire.
- **3.** Ramesh was a brilliant student of class XIth. One day while explaining atomic structure, his teacher used following terms :
  - (i) Spectrum (ii) Emission and absorption spectra (iii) Band and line spectra and (iv) Ion, molecular and atomic spectra.

Ramesh was unable to understand these terms properly, can you explain these terms.

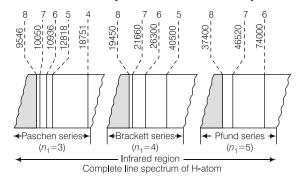
- These terms can be explained as follows :
  - (i) Spectrum A spectrum can be defined as pictorial representation of arrangement of radiations in the increasing order of wavelength or decreasing order of frequency.
  - (ii) Emission and absorption spectra The spectrum of radiation may be emission or absorption on the basis of energy absorbed or emitted.
    - (a) The spectra of radiations emitted by a substance after absorbing energy is called emission spectrum.
    - (b) An absorption spectra is like the photographic negative of an emission spectra. Here a continum of radiations is passed through a sample which absorbs the radiations of certain wavelengths. The missing wavelengths, (which correspond to the radiations absorbed), leave dark spaces in bright continuous spectrum. Such a spectrum is called absorption spectrum.



Jump of hydrogen electron (shown by black circle) from higher energy level to 1st energy level to produce spectral lines of Lyman series. The electronic jumps have been shown in brackets. The electronic jump from  $n_2 = \infty$  to  $n_1 = 1 (\infty \rightarrow 1 \text{ jump})$ has been shown by a dotted arrow.

(iii) Band and line spectra

(a) The emission spectrum of atoms in gaseous phase do not show a continuous spread of wavelengths, here they emit radiations only at specific wavelengths. Such a spectra which contains bright lines with sharp boundaries is called line spectra.



(b) Sometimes in a spectrum very large number of lines are crowded forming a band is called band spectrum. In a band, intensity slowly falls from one end called head of the band. The principle involve in the spectra of atoms or molecule is same as that of line spectrum.

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## AMPLIFIER

- (iv) Ionic, molecular and atomic spectra Emission spectrum can be produced by atom, molecule or ion after absorbing energy. Thus, we can say that atom, molecule and ions emit radiations after being excited, i.e. after absorbing energy and their corresponding spectra are known as ionic, molecular and atomic spectra.
- **4.** What are orbit, subshell and orbitals?
- During our approach to wave mechanical model of atom, we will be coming across three key words about the atom which can be defined according to the probability concept as
  - 1. **Orbit** It is a two dimensional imaginary space around the nucleus where probability of finding electrons is maximum. It can contain 2 to 32 electrons of variable energy, but same family.
  - 2. **Subshell** Aggregation or group of orbitals of exactly similar energy which make an orbit. Subshells are named as *s*, *p*, *d* and *f*.
  - 3. **Orbital** A three dimensional real space around nucleus where probability of finding a particular electron is maximum. An orbital can accommodate maximum of two electrons with exactly equal energy.

This year one question was asked in NEET-Phase II from the above topic, the asked question was

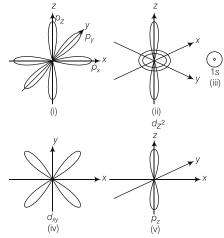
**Ex.** How many electrons can fit in the orbitals for which n = 3 and l = 1?

(a) 10 (b) 14 (c) 2 (d) 6

(c) As mentioned above an orbital can accommodate maximum of two electrons with exactly equal energy but opposite spins.

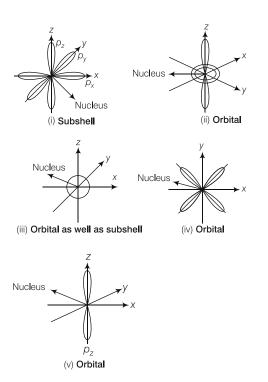
Thus, option (c) is correct.

5. Consider the following pictures,



Mark them as orbital or subshell or both.

Subshell is defined as the aggregation of orbitals of exactly similar energy while orbital is a 3D space around nucleus where probability of finding an electron is maximum. Thus,

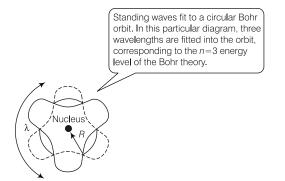


**6.** Seema is an average student of class XIth. That is why her parents sent her in a coaching institute. In first week, coaching teacher was teaching quantum mechanical approach of an atomic structure.

But she was very confused between two terms named as wave function ' $\psi$ ' and probability density ' $\psi$ <sup>2</sup>' and their signs.

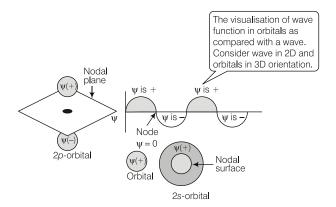
Can you explain these two terms so that she can differentiate between these two terms and choose the correct signs.

(\*) The wavefunction ' $\psi$ ' is regarded as the amplitude function of a 3D electron wave expressed in terms of coordinates *x*, *y* and *z*.



• At any point, wavefunction values may be positive or negative depending upon the values of coordinates.

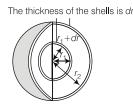
• Its comparison with a wave is given below



- The wavefunction has no direct physical meaning. However, the square of wavefunction,  $\psi^2$ , can be represented in three dimensional region per unit volume of the atom where an electron with a given energy is most likely to be found.
- Schrodinger wave equation gives  $\psi$  values which can be positive as well as negative because these solutions can come in the form of *cos* wave or *sine* wave. If we get *cos* wave as a result, then at 180° our wave function will be negative as cos 180° = -1 but  $\psi^2$  is always positive value. This is because the square of even negative value is positive.
- 7. During a seminar, teachers told students about radial and angular distribution functions. But there are many students who could not understand the difference between these terms. Could you explain the difference between these two terms.
- ③ We shall discuss difference between these two terms one by one as follows:

#### **Radial distribution function**

• This function describes the probability of finding an electron in a spherical shell of atom between the spheres of radius (r + dr) and *r* shown below in the figure.



Volume of a thin shell of thickness *dr* at a radius *r* 

= area of surface of sphere  $\times dr = 4\pi r^2 dr$ 

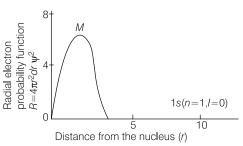
The volume of the thin shell at radius  $r_2$  is greater than that at  $r_1$ .

- These curves tells us about following facts:
- In each case the probability of finding the electrons at the origin is zero.
- The distance for maximum probability in an orbital increases with the value of *n* e.g. distance for 1s, 2s and 3s is in the order 1s < 2s < 3s.

• The total number of peaks appearing in the curves for s, p and d-orbitals is equal to n, (n-1) and (n-2) respectively(n = principal quantum number).

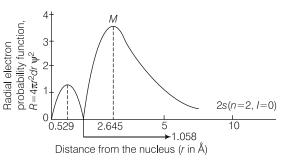
🔊 Amplifier

• The curve of 1s electron is given below



In the above curve we can interpret that the value of R is zero at nucleus where r is also zero. The value of R increases slowly as we move far from the nucleus. It possesses a maximum peak at r = 0.529 Å, which is known as Bohr's radius for first orbit and then it falls to zero as r tends to infinity.

For 2s electron,



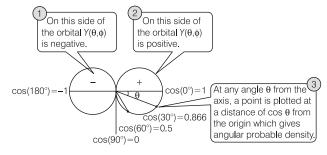
R is zero at r = 0

The point i.e. 1.058 Å at which the probability of finding an electron is zero is called node.

The surface containing the nodes is called nodal plane.

#### Angular distribution function

• This wave function depends upon l and  $m_l$  (independent of n). In more simpler words, these functions give the probability of finding an electron at a certain angle from the nucleus. A better insight of these functions can be get from the figure below



Thus, the structure of atom according to wave mechanical model can be summarised as

• The electrons in an atom are arranged in shell or different energy levels which are indicated by numbers 1, 2, 3, ... or letters *K*, *L*, *M*, ...

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## AMPLIFIER

- Within each shell there are subshells which are designated as *s*, *p*, *d* and *f*.
- Electrons of different energy levels are present in discrete volumes of different shapes, sizes and orientations in the sub-levels around the nucleus.
- Each of such discrete volume is called an orbital which has the maximum probability of finding a particular electron in a particular energy level. The number of orbitals in a subshell is fixed, *s*-subshell has 1, *p* has 3, *d* has 5 and *f* has 7 orbitals.
- Just like the number the shape of orbitals is also fixed i.e. *s* has spherical shape, *p* has dumb bell shape, *d* orbitals have double dumb bell shape while the shape of *f*-orbitals is diffused.
- Each orbital may hold up a maximum of two electrons of exactly equal energy provided they have opposite spins.
- 8. The Schrodinger wave equation for H-atom is

$$\psi_{2s} = \frac{1}{4 \left(2\pi\right)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$
[IIT JEE 2004]

where,  $a_0$  is Bohr's radius. Let the radial node in 2*s* be at  $r_0$ . Then, find *r* in terms of  $a_0$ .

 $\ensuremath{\mathfrak{D}}$  The probability density of finding an electron is zero at radial node.

Hence,  $\psi_{2s}^2$  must be zero at  $r = r_0$ .

Thus, we can find a relationship between  $r_0$  and  $a_0$  by putting  $r = r_0$  and  $\psi_{2s}^2 = 0$ .

$$\psi_{2s}^{2} = \left(\frac{1}{4\sqrt{2\pi}}\right)^{2} \left(\frac{1}{a_{0}}\right)^{3} \left(2 - \frac{r_{0}}{a_{0}}\right)^{2} e^{-r_{0}/a_{0}} = 0$$
  
As  $\frac{1}{4\sqrt{2\pi}}$  and  $e^{-r_{0}/a_{0}}$  cannot be zero, hence  $\left(2 - \frac{r_{0}}{a_{0}}\right)^{2} = 0$   
or  $\frac{r_{0}}{a_{0}} = 2$  or  $r_{0} = 2a_{0}$ 

**9.** Consider the H-atom to be proton embedded in a cavity of radius  $a_0$  (Bohr's radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly.

Estimate the average total energy of an electron in its ground state in a H-atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. [IIT JEE 1996]

- If any process occurs infinitely slow, then we use integration method to find out the asked quantity.
  - In the question, it is provided that total average energy of an electron in its ground state is equal to the work done in the neutralisation process, so we can calculate total average energy as

Total average energy = work done

or 
$$W = -\int_{a_0}^{\infty} F \cdot dr$$
 ...(i)

 $[:: Work = force \times distance]$ 

As process is very slow, so distance is taken dr and proton is embedded from infinite to the, cavity of radius  $a_0$  so limits are taken from  $\infty$  to  $a_0$ . To change limits from  $a_0$  to  $\infty$ , put minus sign in the formula

$$W = -\int_{a_0}^{\infty} \frac{e^2}{4\pi \epsilon_0 r^2} dr \qquad \left[ \because F = \frac{e^2}{4\pi \epsilon_0 r^2} \right]$$

$$W = -\frac{e^2}{4\pi \in_0} \int_{a_0}^{a_0} \frac{1}{r^2} dx$$

or

$$\Rightarrow \qquad W = -\frac{e^2}{4\pi\epsilon_0} \left[ -\frac{1}{r} \right]_{a_0}^{\infty} \qquad \left[ \int \frac{1}{r^2} dr = -\frac{1}{r} + c \right]$$
$$\Rightarrow \qquad W = -\frac{e^2}{4\pi\epsilon_0} \left[ -\frac{1}{\infty} - \left( -\frac{1}{a_0} \right) \right] \qquad \left[ \frac{1}{\infty} = 0 \right]$$

or 
$$W = -\frac{e^2}{4\pi \in_0 a_0} = \text{total energy } (E)$$

Now, if V is magnitude of potential energy, then according to the given information, kinetic energy  $(E_k)$  is  $\frac{V}{2}$ . Therefore,

$$E = -V + \frac{V}{2}$$

(Potential energy is always negative)

$$E = -\frac{V}{2}$$

$$\Rightarrow \qquad V = -2E = -2\left(\frac{-e^2}{4\pi \epsilon_0 a_0}\right)$$

$$= \frac{e^2}{2\pi \epsilon_0 a_0}$$

10. Calculate the energy required to excite 1 L of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol<sup>-1</sup>.

(b) Moles of 
$$H_2 = \frac{pV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.0409$$

(pV = nRT, n =number of moles)

 $\Rightarrow$  Bond energy = 0.0409 × 436 = 17.83 kJ

= 2  $\times$  0.0409  $\times$  6.023  $\times$  10  $^{23}$  = 4.93  $\times$  10  $^{22}$  Transition energy/atom

$$= 2.18 \times 10^{-18} \left( 1 - \frac{1}{4} \right) J$$
$$= \frac{3}{4} \times 218 \times 10^{-18} J$$

 $\Rightarrow$  Total transition energy

4

$$= \frac{3}{4} \times 2.18 \times 10^{-18} \times 4.93 \times 10^{22} \, \text{J}$$

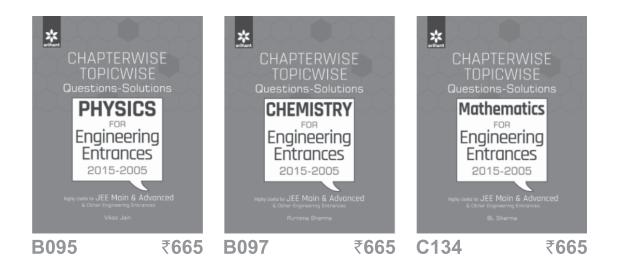
$$= 80.60 \times 10^3 \text{ J} = 80.60 \text{ kJ}$$

Therefore, total energy required

- = Dissociation energy + transition energy
- = (17.83 + 80.60) kJ
- = 98.43 kJ

# CHAPTERWISE TOPICWISE SOLVED PAPERS JEE & OTHER ENGINEERING ENTRANCES

## MASTER COLLECTION OF LAST 10 YEARS' QUESTIONS OF JEE & OTHER ENGINEERING ENTRANCES



## The Highly Useful Resource that will Complement your Preparation as you can use these....

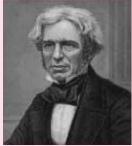
- With Daily Studies as Questions have been given Topicwise.
- For Revision Purpose after the Syllabus is completed.



# \*\*\* FUN ARCADE

## Michael Faraday (1791-1867)

Michael Faraday who gave two important laws for electrolysis, was born in South London in the year 1791 in a poor family. At the age of 13, he left school and started traineeship at a local book binder to help his family's finances. But he was



eager to learn more about the world, he did not restrict himsel binding the books. After working hard each day, he spent his free time reading the books he had bound. In 1812, at the age of 20, he receives some tickets for a series of lectures by the famous scientist Humphery Davy. After the lect Michael sent Davy a 300 page document offering notes on the lect Davy was impressed and he employed Faraday as an chemical assistant at the Royal institution of Great Britain. This later to a Fullerian professor of chemistry at that institution He held this position for the rest of his life.

# CROSSWORD

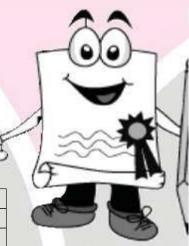
## DOWN

- 1. The ratio of the total mass of a specified element in the earth crust to the total mass of the earth crust.
- 5. A dilute solution of ethanoic acid ( $\approx 6\%$ ), used as a flavouring and pickling medium.
- 6. A substance used to prevent a colloid from coagulating.
- 9. An important component of RNA.
- 10. The chief ore of lead.
- 12. The study of depression in freezing point.
- 13. A colloidal dispersion of a solid or liquid in a gas.
- 16. A solution that resists change in pH.
- 18. It is responsible for coagulation of blood.
- 20. A sugar that has a six membered ring.

## ACROSS

- 2. A colourless organic crystalline compound, made by the reaction of trichloromethanal and chlorobenzene.
- 3. A synthetic rubber made by polymerising the compound 2-chlorobuta-1, 2-diene.
- 4. Material produced during the smelting of metal by reaction of the flux with impurities.
- 7. A range of electromagnetic energies arranged in increasing order of wavelength.
- 8. The heating of a finely ground ore, in air prior to smelting.
- 11. A unit of electric dipole moment.
- 14. A naturally occurring metal sulphide.
- 15. A crystalline solid, used extensively as a reagent for electrophilic addition of bromine.
- 17. A natural or synthetic hydrated alumino silicate with an open 3-D crystal structure.
- 19. A class of mixed metal oxides.

		<sup>6.</sup> S		8.		1.					<sup>10</sup> . G
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18										20.	
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## Chemistr Lipbalms

•Except the lips you protect itself due to easy for your lips to weather and your lip

• If you looked at the side of your favourit find a number of ing These ingredients at of lipbalms. These a respect to scent, flav emollience.

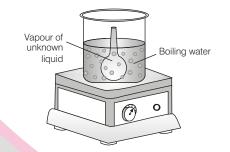
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# **PUZZLES TO PUZZLE YOU**

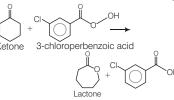
In an experiment done on cockroaches, it was found that male cockroaches were made to run at different speeds on a small scale treadmill, while their oxygen consumption was measured. The average cockroach running at 0.08 km/h consumed 0.8 mL of  $O_2$  at 1 atm pressure and 24°C per gram of insect weight. How many moles of  $O_2$  would be consumed in 1 h by a 5.2 g cockroach moving at this speed? [Ans.  $2 \times 10^{-4}$  mol  $O_2$ ]

Dumas-bulb technique is used to determine the molar mass of an unknown liquid.

In this technique, we vaporise the sample of a liquid that boils below 100°C in a boiling water bath and determine the mass of vapour required to fill the bulb. From the following data, calculate the molar mass of the unknown liquid Mass of unknown vapour = 1.012 g; volume of bulb = 354 cm<sup>3</sup>, pressure = 742 torr and temperature = 99°C [**Ans.** 89.4 g mol<sup>-1</sup>]

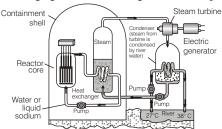


The Baeyer-Villiger reaction is an organic reaction used to convert ketones to lactones, as in the following reaction,



The reactant 3-chloroperbenzoic acid is somewhat shock sensitive and prone to explode. Thus, an alternative process being developed uses hydrogen peroxide and a catalyst consisting of tin deposited within a solid support. What would you expect to be the other product of oxidation of the ketone to lactone by hydrogen peroxide?

The following figure is a basic design of a nuclear power plant.



Why can reactor core not reach super critical levels and explode with the violence of an atomic bomb?

## of ע

r skin produces oil to lack of protective oil, its get dry in hot and cold ps become chapped.

ingredients list on the e lipbalm tube, you gredients written on it. re not same for all types re different with our, creaminess and

e come up with their f ingredients and made choices about which oil and which wax to use in its custom blend to balm.

• If you know the composition of lipbalm, you can make your own. We are providing an idea of percentages of components and their uses which are given below (I) **Emollient carriers** (40-80%) These are solid sunscreen active ingredients that affect the physical and photochemical stability of the product. The most commonly utilised emollient carriers are: Caster seed oil, mineral oil, jojoba seed oil, lanolin, shea butter, petrolatum and octyldodecanal.

Lipbalms are not used as extensively as some of the other personal products. The

reasons for this are the excellent moisturisation and uncountable certain petroleum and animal derived ingredients, the tastelessness of many petroleum derived products and the greater oxidation resistance of the saturated hydrocarbon products.

(ii) Waxes (10-20%)

A range of waxes is used to maintain stick integrity at high, moderate and low temperatures.

(iii) Active ingredients (0-50%) These are used as skin protectants and sun screens.

(iv) Antioxidants (0-0.1%)A very small fraction of antioxidants are

added because our tongue and nose are very sensitive to peroxidation products.

#### (v) Preservatives (0-6%)

The most commonly utilised preservatives in lipbalms are parabens which have a numbing effect on the tongue. So, parabens help reducing the bitterness.

(vi) **Flavour** (0-0.5%) Different flavouring agents ar

Different flavouring agents are added with respect to taste and smell.

(vii) **Photostabilisers** (0-6%) Photostabiliser protects our lips from the harmful rays of sun.



## BEST QUESTIONS ON CHEMICAL & IONIC EQUILIBRIA FOR MEDICAL ENTRANCES

 The metals magnesium and iron can reduce the metal, copper, from a solution having copper ions (Cu<sup>2+</sup>) according to the equilibria

$$Mg (s) + Cu2+ \longrightarrow Mg2+ + Cu(s); K_1 = 6 \times 10^{90}$$
  
Fe(s) + Cu<sup>2+</sup> \low Fe<sup>2+</sup> + Cu(s); K\_2 = 3 \times 10^{26}

Which of the following statements is correct?

- (a) Mg will remove more  $Cu^{2+}$  from solution than Fe
- (b) Fe will remove more  $Cu^{2+}$  from solution than Mg
- (c) Both Mg and Fe will remove  $\mathrm{Cu}^{2+}$  from solution with equal extent
- $(d)\ \mbox{Cannot}$  be predicted
- **2.** A certain buffer solution contains equal concentrations of  $X^-$  and HX. If  $K_b$  for  $X^-$  is  $10^{-10}$ . the pH of the buffer is [CBSE AIPMT 2010] (a) 10 (b) 4 (c) 8 (d) 14
- **3.** Consider the following reaction,

$$2 \operatorname{NH}_3(g) \rightleftharpoons \operatorname{N}_2(g) + 3 \operatorname{H}_2(g)$$
  
The expression for  $K_C$  at 250°C will be

$$(a) K_C = \frac{K_p}{(RT)^2} \qquad (b) K_C = K_p(RT)$$
$$(c) K_p = K_C R \qquad (d) K_C = \frac{K_p}{RT}$$

**4.** For the following reaction,

$$\operatorname{PCl}_5(g) \Longrightarrow \operatorname{PCl}_3(g) + \operatorname{Cl}_2(g)$$

The forward reaction at constant temperature is favoured by

- (a) introducing an inert gas at constant volume
- (b) introducing chlorine gas at constant volume
- (c) introducing an inert gas at constant pressure
- (d) None of the above
- 5. Which of the following combination on mixing equal volumes and concentrations forms a buffer solution?
  (a) NH<sub>4</sub>OH + CH<sub>3</sub>COOH (b) NH<sub>4</sub>Cl + CH<sub>3</sub>COONa
  (c) NH<sub>4</sub>Cl + NH<sub>4</sub>OH (d) NH<sub>4</sub>OH + CH<sub>3</sub>COONa
- 6. Consider the following reactions,

$$\begin{split} \mathbf{N}_2(g) + 3\mathbf{H}_2(g) & \Longrightarrow 2\mathbf{N}\mathbf{H}_3(g) \,; K_1 \\ \mathbf{N}_2(g) + \mathbf{O}_2(g) & \longleftrightarrow 2\mathbf{N}\mathbf{O}(g) \,; K_2 \end{split}$$

$$\mathrm{H}_{2}(g) + \frac{1}{2}\mathrm{O}_{2}(g) \Longrightarrow \mathrm{H}_{2}\mathrm{O}(g) \; ; \; K_{3}$$

The equilibrium constant for

$2 \operatorname{NH}_3(g) + \frac{5}{2} \operatorname{O}_2(g) \rightleftharpoons$	$2 \operatorname{NO}(g) + 3 \operatorname{H}_2 \operatorname{O}(g)$ will be
$(a)  \frac{K_1 K_3}{K_2}$	(b) $\frac{K_1 K_3^2}{K_2}$
$(c)  K_1 K_2 K_3$	$(d)  \frac{K_2 K_3^3}{K_1}$

7. For a hypothetical reaction,

 $\begin{array}{ll} 4A(g) + 5B(g) & \Longleftrightarrow & 4P(g) + 6Q(g) \\ \mbox{The equilibrium constant } K_C \mbox{ has unit} \\ (a) \mbox{ mol}^{-1} \mbox{ L} & (b) \mbox{ mol } \mbox{ L}^{-1} \\ (c) \mbox{ mol}^{-2} \mbox{ L}^{-3} & (d) \mbox{ Unitless} \end{array}$ 

8. Consider the reaction equilibrium,

 $2 \operatorname{SO}_2(g) + \operatorname{O}_2(g) \rightleftharpoons 2 \operatorname{SO}_3(g), \Delta H^\circ = -198 \text{ kJ}$ On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is (*a*) decreasing the temperature and pressure (*b*) decreasing the temperature and increasing the pressure (*c*) increasing the temperature and pressure (*d*) any value of temperature and pressure

9. A vessel contains a mixture of three parts of  $H_2$  and one part of  $N_2$ , gives a mixture containing 10% ammonia (by moles) at equilibrium at 450°C. The total pressure developed in a vessel will be

$$\begin{split} & \mathrm{N}_2(g) + 3\mathrm{H}_2(g) \longrightarrow 2\mathrm{NH}_3(g); K_p = 1.6 \times 10^{-4} \text{ atm} \\ & (a) \ 30.03 \text{ atm} \\ & (b) \ 45.35 \text{ atm} \\ & (c) \ 28.61 \text{ atm} \\ & (d) \ 50.75 \text{ atm} \end{split}$$

10. Consider the following reaction,

 $A(s) + B(g) + \text{Heat} \Longrightarrow 2C(s) + 2D(g)$ 

At equilibrium, pressure B is doubled to restablish the equilibrium. The concentration D is changed by a factor of

$(a)\sqrt{2}$	<i>(b)</i> 2
(c) $2\sqrt{2}$	$(d) \ 3$

**11.** For the reaction,

 $BaO_2(s) \Longrightarrow BaO(s) + O_2(g); \Delta H = + ve$ 

In equilibrium condition, pressure of O<sub>2</sub> depends on [Punjab PMET 2007]

(a) increased mass of BaO

- (b) increased mass of BaO<sub>2</sub>
- (c) increased mass of BaO and BaO 2
  (d) increased temperature at equilibrium
- **12.** For the equilibrium,

 $2NO_2(g) \Longrightarrow N_2O_4(g) + 14.6$  kcal

[UPCPMT 2009]

- (a) favours the formation of N  $_2$ O  $_4$
- (b) favours the decomposition of N  $_2\!{\rm O}_4$
- (c) does not affect equilibrium

The increase in temperature

- (d) stop the reaction
- **13.** Calculate the ionisation constant of 0.1 M weak acid<br/>whose degree of ionisation is 1.134%.<br/>(a)  $2.32 \times 10^{-3}$ <br/>(b)  $1.79 \times 10^{5}$ <br/>(c)  $1.79 \times 10^{-5}$ <br/>(d)  $2.32 \times 10^{3}$
- **14.** If the solubility of AgI in NaI solution is less than that in pure water, which of the following reason is correct ?
  - (a) The temperature of the solution decreases
  - (b) Solubility product of AgI is less than that of NaI
  - (c) Common ion effect

(d) AgI forms complex with NaI

- **15.** If the solubility of AgCl is  $10^{-5} \text{ molL}^{-1}$  then its solubility in 0.1 molar sodium chloride solution is (a)  $10^{-9}$  M (b)  $10^{-8}$  M (c)  $10^{-10}$  M (d)  $10^{-3}$  M
- **16.** The dissociation constants of a weak acid and a weak base constituting the salt are same. The pH of a solution of salt is

(a) less than 7	(b) exactly '
(c) more than 7	(d) zero

**17.** The solubilities of AgCl in H<sub>2</sub>O, 0.01 M CaCl<sub>2</sub>,

 $0.01\,{\rm M}$  NaCl and  $0.05\,{\rm M}$  AgNO\_3 are  $S_1,S_2,S_3$  and  $S_4,$  respectively. The correct relationship among these quantities will be

$(a) S_1 > S_2 > S_3 > S_4$	$(b) S_1 > S_2 = S_3 > S_4$
$(c) S_4 > S_2 > S_3 > S_1$	$(d) S_1 > S_3 > S_2 > S_4$

**18.** The factor by which a 0.2 M solution of sodium acetate be diluted at  $25^{\circ}$ C in order to double the degree of hydrolysis is

(a) two times	(b) four times
(c) six times	(d) eight times

- **19.** If the ratio of concentrations of the salt to the acid is increased by ten times in a mixture of acetic acid and sodium acetate, the pH of the solution
  - (a) decreases by one(b) increases by one(c) decreases ten fold(d) increases ten fold

**20.** Pure ammonia is placed in a vessel at temperature where its dissociation constant is appreciable. At equilibrium,

🔊 medi master bash

(a) concentration of  $H_2$  is less than that of  $N_2$ (b)  $K_p$  does not change significantly with pressure (c) concentration of  $NH_3$  does not change with pressure (d) dissociation constant does not change with pressure

- 21. A sample of Na<sub>2</sub>CO<sub>3</sub> · H<sub>2</sub>O weighing 0.62 g is added to 100 mL of 0.1 N (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. What will be the nature of the resulting solution?
  (a) Acidic
  (b) Neutral
  (c) Basic
  (d) None of these
- **22.** Which of the following reaction is an example of an acid-base reaction?

(a) Al + H<sub>2</sub>O + OH<sup>-</sup>  $\longrightarrow$  AlO<sub>2</sub> +  $\frac{3}{4}$ H<sub>2</sub>

- 23. pH is greater than 8 at equivalence point in which of the following acid-base titrations?
  (a) Acetic acid versus sodium hydroxide
  (b) Acetic acid versus ammonia
  (c) Hydrochloric acid versus ammonia
  - (d) Hydrochloric acid *versus* sodium hydroxide
- **24.** In an aqueous solution of volume 500 mL, when the reaction of  $2 \text{ Ag}^+ + \text{Cu} \rightleftharpoons \text{Cu}^{2+} + 2 \text{ Ag}$  reached equilibrium the  $[\text{Cu}^{2+}]$  was xM. When 500 mL of water was added further, at the equilibrium,  $[\text{Cu}^{2+}]$  would be
  (a) 2xM (b) xM

(c) between xM and (x/2)M (d) less than (x/2)M

**25.** Densities of diamond and graphite are 3.5 g/mL and 2.3 g/mL, respectively. Increase of pressure at the equilibrium

 $C (diamond) \Longrightarrow C (graphite)$ (a) favours backward reaction (b) favours forward reaction (c) increase the reaction rate (d) has no effect

**26.** For the reactions,  $X \Longrightarrow 2Y$  and  $Z \Longrightarrow P + Q$  the equilibrium constants  $K_{p_1}$  and  $K_{p_2}$  are in the ratio of 1 : 9. If the degree of dissociation of X and Z are equal, then the ratio of total pressures at these equilibria is

$$(a) 1:1 (b) 1:36 (c) 1:9 (d) 1:3$$

**27.** A weak acid HX has the dissociation constant  $1 \times 10^{-5}$  M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.01 M solution of NaX is

 $(a) \ 0.1\% \qquad \qquad (b) \ 0.01\% \qquad (c) \ 0.15\% \qquad (d) \ 0.0001\%$ 

## MEDI MASTER BASH

- **28.** Which of the following salts being dissolved in water **36.** For the equilibrium system, gives pH greater than 7 at 25°C? (a) KNO<sub>3</sub> (b) KCN  $(c) \mathrm{NH}_{4}\mathrm{CN}$   $(d) \mathrm{NH}_{4}\mathrm{Cl}$
- **29.** The following equilibrium,

$$P_4(s) + 6Cl_2(g) \iff 4PCl_3(g)$$

is attained by mixing equal moles of P<sub>4</sub> and Cl<sub>2</sub> in an evacuated vessel. Then at equilibrium (a) [Cl<sub>2</sub>] > [PCl<sub>3</sub>]  $(b) [PCl_3] > [P_4]$  $(c)[P_4] > [Cl_2]$ (d) [Cl<sub>2</sub>] > [P<sub>4</sub>]

**30.** 40% of a mixture of 0.2 mole of  $N_2$  and 0.6 mole of  $H_2$ react to give NH<sub>3</sub> according to the equation

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

at constant temperature and pressure. The ratio of the final volume to the initial volume of gases is (a) 7: 10(b) 8:5(c) 4:5(d) 5:4

- **31.** The strong acids generally used as standard solutions in acid-base titrations because
  - (a) the pH at the equivalence point will always be 7
  - (b) they can be used to titrate both strong and weak bases
  - (c) strong acids form more stable solutions than weak acids
  - (d) the salts of strong acids do not hydrolyse
- **32.** 0.1 mole of CH<sub>3</sub>NH<sub>2</sub> having  $K_b$  equal to  $5 \times 10^{-4}$  is mixed with 0.08 mole of HCl and diluted to one litre. The  $[H^+]$  in solution is

(a) $8 \times 10^{-11}$ M	$(b)~8 imes 10^{-5}~{ m M}$
(c) $8 \times 10^{-2}$ M	(d) $1.6 \times 10^{-11} \text{ M}$

- **33.** When ammonia gas dissolves in water to form NH₄OH, water acts as
  - (a) conjugate base
  - (b) an acid
  - (c) a base
  - (d) a non-polar molecule
- **34.** Which of the following relations between equilibrium constant  $(K_p)$  and degree of dissociation ( $\alpha$ ) at a total pressure p for the decomposition of gaseous reaction

$$\mathrm{H}_2\mathrm{O}(g) \iff \mathrm{H}_2(g) + \frac{1}{2}\mathrm{O}_2(g)$$

is correct?

$$\begin{aligned} (a) \ K_p &= \frac{\alpha^3 p^{1/3}}{(1+\alpha) \ (2+\alpha)^{1/2}} \quad (b) \ K_p &= \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha) \ (2+\alpha)^{1/2}} \\ (c) \ K_p &= \frac{\alpha^3 p^{3/2}}{(1-\alpha) \ (2+\alpha)^{1/2}} \quad (d) \ K_p &= \frac{\alpha^{3/2} p^2}{(1-\alpha) \ (2+\alpha)^{1/2}} \end{aligned}$$

[Kerala CEE 2007]

- **35.** According to theory of active mass, the rate of chemical reaction is directly proportional to
  - (a) volume of apparatus
  - (b) equilibrium constant
  - (c) concentration of reactants
  - (d) properties of reactant

$$H_2 + I_2 \Longrightarrow 2 HI$$

If the concentration of the reactants at 25°C is increased, the value of  $K_C$  will

(a) increase

(b) decrease

(c) depends on the nature of the reactants

- (d) remains the same
- **37.** Which of the following is the correct relation between hydrolysis constant and dissociation constant for  $MgCl_2$ ?

$$(a) K_{h} = \frac{K_{w}}{K_{a}}$$

$$(b) K_{w} = \frac{K_{h}}{K_{b}}$$

$$(c) K_{h} = \frac{K_{w}}{K_{b}}$$

$$(d) K_{h} = \frac{K_{w}}{K_{a} \times K}$$

- **38.** The pH at equivalence point in the titration of 0.1 M CH<sub>3</sub>COOH and 0.1 M NaOH if  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$  is
  - (a) 7(b) between 6 and 7 (c) between 7 and 8 (d) between 8 and 9
- **39.** Which among the following reactions is favoured to proceed in forward direction by increase in temperature ?  $(a) \operatorname{N}_{2}(g) + \operatorname{3H}_{2}(g) \rightleftharpoons 2\operatorname{NH}_{3}(g) + 22.9 \operatorname{kcal}$ (b) N<sub>2</sub> $(g) + O_2(g) \implies 2$ NO(g) - 42.8 kcal (c)  $2\text{SO}_2(g) + \text{O}_2(g) \implies 2\text{SO}_3(g) + 45.3$  kcal (d) H<sub>2</sub> $(g) + Cl_2(g) \Longrightarrow 2HCl(g) + 44$  kcal
- **40.** The value of  $K_p$  for the reaction,

$$N_2(g) + 3H_2(g) \Longrightarrow 2NH_3(g)$$

is  $4.28 \times 10^{-5} \text{atm}^{-2}$  at 725K. The partial pressures of N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub> are 2 atm, 1 atm and 3atm, respectively in the reaction mixture.

The direction in which the net reaction proceed will be

- (a) forward (b) backward (c) direction cannot be predicted
- (d) no net reaction
- **41.** Which of the following combinations of  $BaCl_2$  and NaF containing equal volumes will not give a precipitate? ( $K_{sp}$  of BaF<sub>2</sub> = 1.7 × 10<sup>-7</sup>). (*a*) 10<sup>-3</sup> M BaCl<sub>2</sub> and 2×10<sup>-2</sup> M NaF (b)  $10^{-3} \ \mathrm{M} \ \mathrm{BaCl}_2$  and  $1.5{\times}10^{-2} \ \mathrm{M} \ \mathrm{NaF}$ (c)  $1.5 \times ~10^{-2} \ \mathrm{M} \ \mathrm{BaCl}_2$  and  $10^{-2} \ \mathrm{M} \ \mathrm{NaF}$ 
  - (d)  $2 \times 10^{-2} \text{ M BaCl}_2$  and  $2 \times 10^{-2} \text{ M NaF}$
- **42.** The equilibrium constant for the dissociation of the following two complexes is
  - (I)  $K_4[Fe(CN)_6] \rightarrow 2.6 \times 10^{37}$
  - (II)  $K_3[Fe(CN)_6] \rightarrow 1.9 \times 10^{17}$

- (a) I and II are equally stable
- (b) I is more stable than II
- (c) II is more stable than I
- (d) Unpredictable stability
- **43.** A vessel contains carbon dioxide at 1000 K temperature and 0.5 atm pressure. On addition of graphite some of the carbon dioxide is converted to carbon monoxide. The total pressure at equilibrium is 0.8 atm then the value of  $K_p$  is

(a) 1.8 atm (b) 2.2 atm (c) 3.5 atm (d) 7.2 atm

**44.** The figure given below shows plot of  $\ln K_{eq}$  versus 1/Tfor a reaction. The reaction is



- (a) exothermic
- (b) endothermic
- (c) one with negligible enthalpy change
- (d) highly spontaneous at ordinary temperature
- **45.** The equilibrium constants for the following reactions are given as

$$\begin{split} & \mathrm{N}_{2}(g) + \mathrm{O}_{2}(g) \mathop{\longrightarrow}\limits^{} 2\mathrm{NO}(g); \ K_{1} \\ & \mathrm{NO}(g) \mathop{\longrightarrow}\limits^{} \frac{1}{2}\mathrm{N}_{2}(g) + \frac{1}{2}\mathrm{O}_{2}(g); \ K_{2} \end{split}$$

Which of the following relation between  $K_1$  and  $K_2$  is correct?

(a) 
$$K_1 = \frac{1}{K_2^2}$$
 (b)  $K_1 = K_2^2$  (c)  $K_1 = \frac{1}{K_2}$  (d)  $K_1 = (K_2)^0$ 

**46.** The value of  $\Delta G^{\circ}$  for the decomposition of  $NH_4Cl(s)$ at 25°C if  $K_p$  =1  $\times 10^{-16}$  is

(b) 91 kJ (a) 91 J(c) 9.1 kJ (d) 910 kJ

**47.** Match the Column I with Column II and choose the correct option.

Bi	ismu lumi	th (l	phosph III) sulp n hydro	ohide			р. q.	$^{2}$	$ \frac{08x^5}{7x^4} $ $ x^3 $
A	lumi						q.	_	
		niun	n hydro	xide					0
					Aluminium hydroxide				
	Calcium fluoride					s.	6	$912x^{2}$	
es									
A	В	С	D			Α	В	С	D
q	$\mathbf{s}$	р	r		<i>(b)</i>	$\mathbf{s}$	р	q	r
r	р	$\mathbf{s}$	q		(d)	$\mathbf{s}$	q	р	r
•	es A A	e <b>s</b> A B q s	es ABC qsp	es A B C D q s p r	es A B C D q s p r	es A B C D A s p r (b)	es A B C D A A s p r (b) s	es A B C D A B A s p r (b) s p	es ABCD ABC qspr (b)spq

- **48.** The solution is made acidic for the precipitation of second group cations because
  - (a) the  $S^{2-}$  ion concentration should increase
  - (b) the  $S^{2-}$  ion concentration should decrease
  - (c) the hydrogen ion concentration should increase
  - (d) the degree of dissociation of HCl should decrease

## 🕅 MEDI MASTER BASH

- **49.** 0.01 mole of lime (CaO) was dissolved in 100 cm<sup>3</sup> of water. Assuming the base is completely ionised in the solution, the pH of the solution will be (a) 8.5(b) 8(c) 6(d) 13.3
- **50.** 0.1 mole of  $N_2O_4$  was sealed in a tube under one atmospheric conditions at 25°C. Calculate the number of moles of  $NO_2(g)$  present, if the equilibrium  $N_2O_4(g) \longrightarrow 2NO_2(g)$  ( $K_p = 0.14$ ) is reached after some time (a) 0.036(d) 3.600

*(b)* 36.00 (c) 360.0

## Answers

<ol> <li>(a)</li> <li>(d)</li> <li>(d)</li> <li>(d)</li> <li>(b)</li> </ol>	<ol> <li>(b)</li> <li>(b)</li> <li>(b)</li> <li>(c)</li> <li>(c)</li> </ol>	<ol> <li>(a)</li> <li>(b)</li> <li>(c)</li> <li>(b)</li> </ol>	<ol> <li>4. (c)</li> <li>9. (a)</li> <li>14. (c)</li> <li>19. (b)</li> </ol>	<ol> <li>5. (c)</li> <li>10. (a)</li> <li>15. (a)</li> <li>20. (b)</li> </ol>
21. (a)	22. (b)	<ul> <li>23. (a)</li> <li>28. (b)</li> <li>33. (b)</li> <li>38. (d)</li> </ul>	24. (d)	25. (c)
26. (b)	27. (b)		29. (c)	30. (c)
31. (b)	32. (a)		34. (b)	35. (c)
36. (d)	37. (c)		39. (b)	40. (b)
<b>41.</b> (c)	<b>42.</b> (c)	<b>43.</b> (a)	<b>44.</b> (a)	<b>45.</b> (a)
<b>46.</b> (b)	<b>47.</b> (b)	<b>48.</b> (b)	<b>49.</b> (d)	<b>50.</b> (a)

# **Complete Preparation for** BITSAT 20





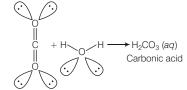
#### Why do the oxides of metals form basic solution and oxides of non-metals form acidic solution with water?

In order to understand the explanation of this question, you must know the difference between hydration and hydrolysis.

**Hydration** When any substance is dissolved in water, the constituent particles of this substance become surrounded by water molecules. This process of surrounding these constituent particles with water is called *hydration* and the ions formed are called *aquo-ions*.

e.g.  $\operatorname{NaCl}(s) + \operatorname{H}_2O(I) \longrightarrow \operatorname{Na}^+(aq) + \operatorname{Cl}^-(aq)$ 

**Hydrolysis** In the continuation of hydration process, the constituent particles may react with water. The reaction of these particle is called *hydrolysis*. Hydrolysis always lead to a change in pH of the solution because the relative number of hydroxonium or hydroxide ions is changed. e.g.



 $H_2CO_3(aq) + H_2O(l) \longrightarrow H_3O^+ + HCO_3^-(aq)$ 

Metals on the left of the periodic table typically have basic oxides, e.g. the reaction between magnesium oxide and water, gives magnesium hydroxide. Magnesium hydroxide is soluble in water and produces an alkaline solution of pH about 10.

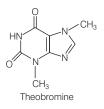
 $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s) \implies Mg^{2+}(aq) + 2\bar{O}H(aq)$ 

Non-metals on the right of the periodic table typically have acidic oxides. e.g.  $SO_3$  reacts with water and produces a strongly acidic solution of sulphuric acid. Sulphuric acid dissociates, producing H<sup>+</sup> ions, which increases the acidity of the solution.

$$SO_3(g) + H_2O(I) \longrightarrow H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

#### Small amounts of chocolate can kill your dog.

Chocolate contains an alkaloid named as **theobromine**. Theobromine is a mild stimulant, has the same effect as caffeine.



Theobromine does not show any harmful effects to human on consumption because humans easily metabolise it. But some animals like dogs, cats and horses, metabolise theobromine slowly, allowing it to build upto toxic levels in their systems.

The ill effects of chocolate to your dog depend on the types of chocolate and your dog's size.

Cocoa, cooking chocolate and dark chocolate contain highest level of theobromine, while milk chocolate and white chocolate have the lowest.

Thus, small amount of dark chocolates takes less time to poison a dog. Less than 28 g of a dark chocolate may be enough to poison a 20 kg dog.

The noticable side effects of theobromine in dogs includes, diarrhea, vomiting, increased urination, tremors, irregular heartbeats etc.

Some of these symptoms, can ultimately kill your dog.

Treatments Induce vomiting immediately to remove excess quantity of chocolate.

Try to get dog to eat small amount of activated charcoal, which binds to the theobromine and does not allow it to enter the blood stream.

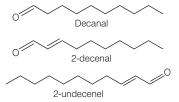
Try to get the dog to consume more water in order to keep them hydrated.

#### Why do some people feel coriander taste soapy?

In your homes, often you see that coriander leaves are used in order to enhance the taste of food. But there are some people who found taste of coriander unpleasent and soapy. The cause of this lies in the chemical composition of coriander leaves.

The coriander leaves composed of around 40 different organic compounds. Out of these compounds, 82% of these are aldehydes and 17% alcohols.

The aldehydes mainly with 9-10 C-atoms, are responsible for the soapy taste for some people. These aldehydes are also commonly found in both soaps and lotions.



However, its certainly not just the chemical composition of coriander leaves that makes some people finds it has soapy taste. It's been suggested that there is also a genetic basis to this, which explains why not everyone has the same taste.

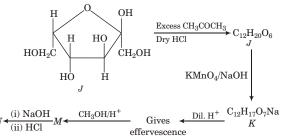
Scientists have highlighted a specific gene that codes for a receptor that is highly sensitive to the flavour of aldehydes. Several other genes have also been linked, however, it seems likely that more than one could be responsible.

As well as it is also possible for people to grow to like the taste of coriander, with it being suggested that repeated exposure to the taste leads to the brain for giving new positive associations.



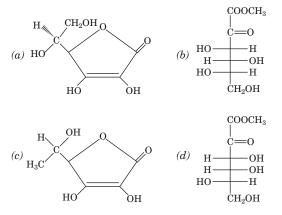
To boost up your rank in JEE Main and Advanced

- An electron is moving in the Bohr's first orbit of a H-atom. What is the ratio of its velocity to the velocity of light in a vacuum?
  (a) 137 (b) 155 (c) 132 (d) 123
- 2. Consider the following reaction sequence,





What is the structure of N?



3. In a process for water proofing, a fabric is exposed to (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> vapour. The vapour reacts with hydroxyl groups on the surface of the fabric or with traces of water to form the water proofing film [(CH<sub>3</sub>)<sub>2</sub>SiO]<sub>n</sub>, by the reaction, 
$$\begin{split} n\,(\mathrm{CH}_3)_2\,\mathrm{SiCl}_2\,+\,2n\,\bar{\mathrm{O}}\,\mathrm{H} \longrightarrow 2n\mathrm{C}\bar{\mathrm{I}}+n\mathrm{H}_2\mathrm{O} \\ &+\left[(\mathrm{CH}_3)_2\,\mathrm{SiO}\right]_n \end{split}$$

where, *n* stands for a large integer. The water proofing film is deposited on the fabric layer. Each layer is 6.0 Å thick (the thickness of the  $(CH_3)_2$  SiO group).

How much  $(CH_3)_2 SiCl_2$  is needed to water proof one side of a piece of fabric, 1.00 m by 3.00 m, with a film 300 layers thick?

(The density of the film is 1.00 g/cm<sup>3</sup>) (a) 0.94 g (b) 0.84 g (c) 0.74 g (d) 0.89 g

- 4. In an autoengine with no pollution controls 5% of the fuel (assume 100% octane, C<sub>8</sub>H<sub>18</sub>)is unburned. The relative masses and the relative volumes of CO and C<sub>8</sub>H<sub>18</sub> emitted in the exhaust gas will be (a) 37 and 1.5×10<sup>2</sup>
  (b) 32 and 2.5×10<sup>2</sup>
  (c) 35 and 1.5×10<sup>2</sup>
  (d) 38 and 1.7×10<sup>2</sup>
- 5. In solid ammonia, each NH<sub>3</sub> molecule has six other NH<sub>3</sub> molecules as nearest neighbours.  $\Delta H$  of sublimation of NH<sub>3</sub> at the melting point is 30.8 kJ/mol and the estimated  $\Delta H$  of sublimation in the absence of hydrogen bonding is 14.4 kJ/mol. The strength of a hydrogen bond in solid ammonia would be (a) 6.5 kJ/mol (b) 5.5 kJ/mol (c) 7.5 kJ/mol (d) 8.5 kJ/mol
- 6. A certain liquid has a viscosity of  $1.00 \times 10^4$  poise and a density of 3.2 g/mL. How long will it take for a platinum ball with a 2.5 mm radius to fall 1.00 cm through the liquid?

(The density of platinum is 21.4 g/cm<sup>3</sup>). (a) 30 s (b) 40.5 s (c) 50.5 s (d) 55.5 s

## BRAIN TEASERS

**7.** The thermochemical equation for the combustion of ethylene gas,  $C_2H_4$  is

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l);$$

 $\Delta H^{\circ} = -337 \text{ kcal/mol}$ 

Assuming 70% efficiency, how many kilogram of water at 20°C can be converted into steam at 100°C by burning 1.00 m<sup>3</sup> of  $C_2H_4$  gas measured at STP? (*a*) 20.9 kg (*b*) 16.9 kg (*c*) 15.7 kg (*d*) 17.9 kg

8. A virus preparation was inactivated in a chemical bath. The inactivation process was found to be first order with respect to virus concentration and at the beginning of the experiment 2% of the virus was found to be inactivated per minute. The value of *k* for the inactivation process would be

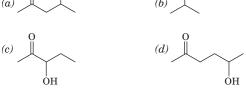
 $\begin{array}{l} (a) \ 3.3 \ \times \ 10^{-4} \ {\rm s}^{-1} \\ (b) \ 2.2 \ \times \ 10^{-4} \ {\rm s}^{-1} \\ (c) \ 2.5 \ \times \ 10^{-4} \ {\rm s}^{-1} \\ (d) \ 5.5 \ \times \ 10^{-4} \ {\rm s}^{-1} \end{array}$ 

- 9. If 50.0 mL of a solution containing 0.0010 mole of silver ion, is mixed with 50.0 mL of 0.100 M HCl solution, how much silver ion remains in solution?  $(K_{sp} = 1 \times 10^{-10})$ (*a*)  $2 \times 10^{-10}$  mol (*b*)  $2.5 \times 10^{-10}$  mol (*c*)  $3.5 \times 10^{-10}$  mol (*d*)  $4 \times 10^{-10}$  mol
- 10. Assuming a constant concentration of 10.0 M H<sub>2</sub>SO<sub>4</sub>, the energy obtainable from a lead storage battery in which 0.100 mole of lead is consumed would be (a) 42.8 kJ (b) 45.5 kJ (c) 40.5 kJ (d) 42.2 kJ
- A Tl<sup>+</sup>/Tl couple was prepared by saturating 0.100 M KBr with TlBr and allowing the Tl<sup>+</sup> from the relatively insoluble bromide to equilibrate. This couple was observed to have a potential of 0.443 V with respect to a Pb<sup>2+</sup> /Pb couple in which Pb<sup>2+</sup> was 0.100 M. What is the solubility product constant of TlBr?
  - $\begin{array}{l} (a) \ 6 \times 10^{-6} \\ (b) \ 3 \times 10^{-6} \\ (c) \ 3.6 \times 10^{-6} \\ (d) \ 4 \times 10^{-6} \end{array}$
- **12.** An organic compound X with molecular formula,  $C_7H_8O$  is insoluble in  $aq \cdot NaHCO_3$

but dissolves in NaOH. When treated with bromine water, X rapidly gives Y,  $C_7H_5OBr_3$ . The compound X and Y, respectively are

- (a) benzyl alcohol and 2, 4, 6-tribromo-3-methoxybenzene (b) benzyl alcohol and 2, 4, 6-tribromo-3-methylphenol
- (c) o-cresol and 3, 4, 5-tribromo-2-methylphenol
- (d) m-cresol and 2, 4, 6-tribromo-3-methylphenol

dehydrated in acidic condition? O OH OH (a) || || || || || || ||



**13.** Which one of the following will most readily be

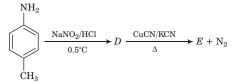
**14.** A particular 100 octane aviation gasoline used 1.00 cm<sup>3</sup> of tetraethyl lead  $(C_2H_5)_4Pb$ , of density 1.66 g/cm<sup>3</sup>, per litre of product. This compound is made as follows:

 $4C_{2}H_{5}Cl + 4NaPb \longrightarrow (C_{2}H_{5})_{4}Pb + 4NaCl + 3Pb$ 

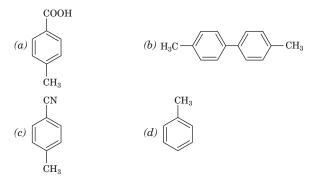
How many grams of ethyl chloride,  $C_2H_5Cl$ , is needed to make enough tetraethyl lead for 1.00 L of gasoline?

- (a) 1.33 g (b) 2.30 g (c) 2.50 g
- (c) 2.50 g (d) 3.5 g

**15.** In the reaction,



The product E is

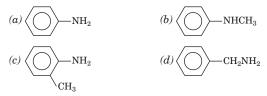


**16.**  $RNH_2$  reacts with  $C_6H_5SO_2Cl$  in  $aq \cdot KOH$  to give a clear solution. On acidification, a precipitate is obtained which is due to the formation of

$$\begin{array}{c} & H \\ | \\ (a) R - N^{+} - SO_{2}C_{6}H_{5}OH \\ | \\ H \\ (c) C_{6}H_{5}SO_{2}NH_{2} \end{array} (b) R - \bar{N}SO_{2}C_{6}H_{5}K^{+} \\ (d) R - NH - SO_{2} - C_{6}H_{5} \\ \end{array}$$

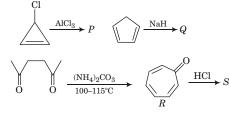
# **BRAIN TEASERS**

**17.** Which of the following is the strongest base?



- 18. The reaction of white phosphorus with *aq*. NaOH gives phosphine alongwith another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product, respectively are
  - (a) redox reaction, -3 and -5
  - (b) redox reaction, +3 and +5
  - (c) disproportion reaction, -3 and +5
  - (d) disproportionation reaction, –3 and +3
- **19.** Between  $SiCl_4$  and  $CCl_4$ , only  $SiCl_4$  reacts with water because
  - (a) SiCl<sub>4</sub> has vacant *d*-orbitals available with Si
  - (b)  $SiCl_4$  is covalent
  - $(c)\operatorname{SiCl}_4$  is ionic, while  $\operatorname{CCl}_4$  is covalent
  - $(d)\operatorname{SiCl}_4$  has bigger size than that of  $\operatorname{CCl}_4$

#### **20.** Among *P*, *Q*, *R* and *S*,



the aromatic compounds(s) is/are (a) P and Q (b) Q and R(c) R and S (d) P, Q, R and S

**21.** What is the decreasing order of strength of the following bases?

$$\begin{split} \bar{\mathrm{OH}} &, \bar{\mathrm{NH}}_2, \mathrm{H-\!\!-\!C} \equiv \bar{\mathrm{C}} \text{ and } \mathrm{CH}_3 - \bar{\mathrm{CH}}_2 \\ \text{(a) } \mathrm{CH}_3 - \bar{\mathrm{CH}}_2 > \bar{\mathrm{NH}}_2 > \mathrm{H-\!\!-\!C} \equiv \bar{\mathrm{C}} > \bar{\mathrm{OH}} \\ \text{(b) } \mathrm{H-\!\!-\!C} \equiv \bar{\mathrm{C}} > \mathrm{CH}_3 - \bar{\mathrm{CH}}_2 > \bar{\mathrm{NH}}_2 > \bar{\mathrm{OH}} \\ \text{(c) } \bar{\mathrm{OH}} > \bar{\mathrm{NH}}_2 > \mathrm{H-\!\!-\!C} \equiv \bar{\mathrm{C}} > \mathrm{CH}_3 - \bar{\mathrm{CH}}_2 \\ \text{(d) } \bar{\mathrm{NH}}_2 > \mathrm{H-\!\!-\!C} \equiv \bar{\mathrm{C}} > \bar{\mathrm{OH}} > \mathrm{CH}_3 - \bar{\mathrm{CH}}_2 \end{split}$$

**22.**  $A_1$  and  $A_2$  are two ores of metal M.  $A_1$  on calcination gives black precipitate, CO<sub>2</sub> and water.

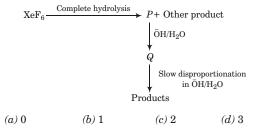
$$A_{1} \xrightarrow{\text{Calcination}} \text{Black solid} + \text{CO}_{2} + \text{H}_{2}\text{O}$$

$$A_{1} \xrightarrow{\text{Dil. HCl}} \text{I}_{2} + \text{ppt.}$$

$$A_{2} \xrightarrow{\text{Roasting}} \text{Metal} + \text{Gas}$$

$$\downarrow \text{K}_{2}\text{Cr}_{2}\text{O}_{7} + \text{H}_{2}\text{SO}_{4}$$
Green colour

- Ores  $A_1$  and  $A_2$  are  $(a) \operatorname{Cu}(\operatorname{OH})_2 \cdot \operatorname{CuCO}_3$  and  $\operatorname{Cu}_2 S$   $(b) \operatorname{CuCl}_2$  and  $\operatorname{CuI}$   $(c) \operatorname{CuCO}_3$  and  $\operatorname{Cu}_2 S$  $(d) \operatorname{Cu}_2 S$  and  $\operatorname{Cu}(\operatorname{OH})_2$
- **23.** Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is



24. Which of the following compounds is not yellow coloured?(a) Zn<sub>2</sub>[Fe(CN)<sub>6</sub>]

$$\begin{array}{l} (b)\,K_3[{\rm Co(NO_2)_6}] \\ (c)\,({\rm NH_4})_3[{\rm As}({\rm Mo_3O_{10}})_4\,] \\ (d)\,{\rm BaCrO_4} \end{array}$$

- **25.** Sulphur melts to a clear mobile liquid at 119°C, but on further heating above 160°C, it becomes viscous due to
  - (a) formation of long chain molecules of sulphur gets entangled into each other
  - $(b) \;\; {\rm breaking \; of \; sulphur \; ring \; and \; formation \; of \; linear \; chain \;}$
  - $(c) \;\;$  formation of eight membered puckered ring structure
  - (d) rhombic structure of sulphur



The origin of biogas is traced back to the Persians. They discovered that organic matter such as rotting vegetables gave of a flammable gas that could be used for other purposes. Around 2000 to 3000 years ago, Marco Polo wrote about the use of covered sewage tanks in Ancient China. We Indians built the first sewage plant in Bombay to make use of this biogas way back in 1859. This idea was then adopted in the UK in 1895, where it was used to light up street lamps.

# **Answers** with **Explanation**

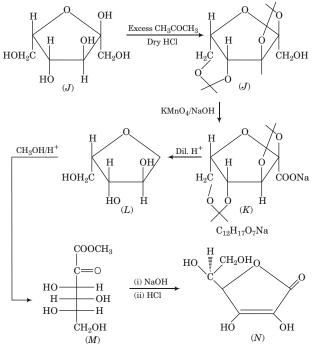
1. (a) KE = 
$$\frac{KZe^2}{2r} = \frac{mv^2}{2}$$
  
 $\frac{KZe^2}{r} = mv^2$   
 $v = \frac{\sqrt{KZ} \cdot e}{\sqrt{m \cdot r}} = \frac{\sqrt{KZ} \cdot e}{\sqrt{m}\sqrt{\frac{n^2h^2}{4\pi^2KZme^2}}} = \frac{2\pi KZ \cdot e^2}{nh}$ 

For hydrogen,

$$\begin{split} v_1 &= \frac{2(3.14)(9.00\times10^9 \,\mathrm{Jm/C^2})(1)(1.60\times10^{-19} \mathrm{C})^2}{1(6.63\times10^{-34} \mathrm{~Js})} \\ &= 2.18\times10^6 \mathrm{~m/s} \\ \frac{c}{v_1} &= \frac{3.00\times10^8 \mathrm{~m/s}}{2.18\times10^6 \mathrm{~m/s}} = 137 \end{split}$$

Light travels 137 times as fast as the electron in this orbit.

#### **2.** (a)



3. (a) Mass of film = Volume of film × density of film
= (area of film)×(thickness of film) × (density of film)
= (100 cm× 300 cm)(300× 6.0 Å)

 $(10^{-8} \text{ cm} / \text{ Å})(1.0 \text{ g} / \text{ cm}^3)$ 

= 0.54 g

The equation involves n moles each of  $(\rm CH_3)_2SiCl_2$  and  $[(\rm CH_3)_2SiO].$ 

Therefore, 1 mole (74 g) of  $(CH_3)_2$ SiO in the film requires 1 mole (129 g) of  $(CH_3)_2$ SiCl<sub>2</sub>. Then, 0.54 g of  $(CH_3)_2$ SiO requires  $(0.54 \text{ g})(129/74) = 0.94 \text{ g} (CH_3)_2$ SiCl<sub>2</sub>.

4. (a) 
$$2C_8H_{18} + 17O_2 \longrightarrow 16CO + 18H_2O_2$$

Per mole of fuel 0.05 is unreacted and 
$$(0.95 \text{ mol}) \left( \frac{16 \text{ mol CO}}{2 \text{ mol } C_8 H_{18}} \right) = 7.6 \text{ moles of CO is produced.}$$

Since, the temperatures and pressures of the two gases are the same, the volume ratio equals the mole ratio  $\overline{5.2}$ 

= 37

$$\frac{7.6 \text{ mol CO}}{0.05 \text{ mol C}_8 \text{H}_{18}} = 1.5 \times 10^2$$

The mass ratio of CO and  $C_8 H_{18}$   $= \frac{(7.6 \ mol \ CO)(28.0 \ g \ / mol)}{(0.05 \ mol \ C_8 H_{18})(114 \ g \ / mol)}$ 

5. (b) Total strength of all hydrogen bonds

= 16.4 kJ/mol

There are 6 nearest neighbours, but each hydrogen bond involves 2 molecules. Thus, the total strength is obtained by dividing  $\frac{6}{2} = 3$ , i.e.  $\frac{16.4}{3}$  kJ/mol = 5.5 kJ/mol.

(b) The mass of the platinum ball and of the liquid it displaces are determined from the respective densities and the volume of the ball.Volume is given by

$$V = \frac{4}{3}\pi r^{3} = \frac{4}{3}(3.14)(0.25 \text{ cm})^{3}$$

$$= 0.0654 \text{ cm}^{3}$$

$$m (\text{Pt}) = (0.0654 \text{ cm}^{3})(21.4 \text{ g/cm}^{3}) = 1.40 \text{ g}$$

$$m_{0} (\text{liquid}) = (0.0654 \text{ cm}^{3})(3.2 \text{ g/cm}^{3}) = 0.21 \text{ g}$$

$$v = \frac{(m - m_{0})\text{g}}{6\pi r \eta}$$

$$= \frac{(1.40 \text{ g} - 0.21 \text{ g})(980 \text{ cm/s}^{2})}{6(3.14)(0.25 \text{ cm})(1.00 \times 10^{4} \text{ poise})}$$

$$= 2.47 \times 10^{-2} \text{ cm/s}$$

$$\text{Time } (t) = \frac{\text{Displacement } (d)}{\text{Velocity } (v)}$$

$$= \frac{1.00 \text{ cm}}{2.47 \times 10^{-2} \text{ cm/s}} = 40.5 \text{ s}$$
7. (b)  $n(\text{C}_{2}\text{H}_{4}) = \frac{(1.00 \text{ m}^{3})(1000 \text{ L} / \text{m}^{3})}{22.4 \text{ L} / \text{ mol}} = 44.6 \text{ mol}$ 

$$\Delta H (1 \text{ m}^{3}) = n(\text{C}_{2}\text{H}_{4}) \times \Delta H (1 \text{ mol})$$

$$= (44.6 \text{ mol})(-337 \text{ kcal}/\text{mol})$$

$$= 1.05 \times 10^{4} \text{ kcal}$$
The useful heat is then  $(0.700) (1.50 \times 10^{4} \text{ kcal})$ 

$$= 1.05 \times 10^{4} \text{ kcal}$$
For the overall process, consider two stages
$$H_{2}O (l, 20^{\circ}\text{C}) \longrightarrow H_{2}O (l, 100^{\circ}\text{C})$$

$$\Delta H = (1.00 \text{ kcal} / \text{ kg K})(80 \text{ K}) = 80 \text{ kcal/kg}$$

$$\begin{array}{l} \mathrm{H_2O}(l,\,100^\circ\mathrm{C}) \longrightarrow \mathrm{H_2O}(\,g,\,100^\circ\mathrm{C}) \ \Delta H = 540 \ \mathrm{kcal/kg} \\ \Delta H(\mathrm{total}) = 80 \ \mathrm{kcal/kg} \end{array}$$

# **BRAIN TEASERS**

The mass of water converted is then equal to the amount of heat available divided by the heat requirement per kg.

$$m({\rm H}_{2}{\rm O}) = \frac{1.05 \times 10^{4} \text{ kcal}}{620 \text{ kcal/ kg}}$$

8. (a) From the first order rate law,

k

$$= -\frac{\Delta[A]}{[A]}\frac{1}{\Delta t}$$

It is seen that only the fractional change in concentration,  $-\Delta[A]/[A]$ , is needed; namely, 0.020, when  $\Delta t = 1$  min = 60 s.

This form of the equation may be used for the initial rate, when the value of [A] is not changing appreciably; that condition is certainly met when only 2% is inactivated in the first minute.

$$k = \frac{0.020}{60\,\mathrm{s}} = 3.3 \times 10^{-4}\,\mathrm{s}^{-1}$$

(b) The initial quantity of Cl<sup>-</sup> ion is given by (50.0 mL) (0.100 mmol/L) = 5.00 mmol = 0.00500 mol Cl<sup>-</sup>. At equilibrium, let x = number of mole of silver ion remaining in solution.

Therefore, 0.0010 - x = 0.0010 mole of silver ion and an equal fraction of a mole of chloride ion have precipitated, leaving 0.0040 mole of chloride ion remaining in solution. The total volume of the solution is 100.0 mL.

$$[Cl^{-}] = \frac{0.0040 \text{ mol}}{0.100 \text{ L}} = 0.040 \text{ M}$$
$$K_{sp} = [Ag^{+}][Cl^{-}] = [Ag^{+}][0.040]$$
$$= 1 \times 10^{-10}$$
$$[Ag^{+}] = \frac{1 \times 10^{-10}}{0.040} = 2.5 \times 10^{-9} \text{ M}$$
$$x = (2.5 \times 10^{-9} \text{ mol} / \text{L})(0.100 \text{ L})$$
$$= 2.5 \times 10^{-10} \text{ mol}$$

**10.** (a) PbO<sub>2</sub> + 4H<sup>+</sup> + SO<sub>4</sub><sup>2-</sup> + 2e<sup>-</sup>  $\longrightarrow$ 

$$PbSO_4 + 2H_2O; E^\circ = 1.70 V$$

 $\begin{array}{l} \operatorname{Pb} + \operatorname{SO}_4^{2-} \longrightarrow \operatorname{PbSO}_4 + 2e^-; E^\circ = 0.31 \text{ V} \\ \operatorname{PbO}_2 + \operatorname{Pb} + 4 \text{ H}^+ + 2 \operatorname{SO}_4^{2-} \longrightarrow \end{array}$ 

$$\begin{split} & 2 \text{PbSO}_4 + 2 \text{H}_2 \text{O}; E^\circ = 2.01 \text{ V} \\ E &= E^\circ - \left(\frac{0.0592}{2}\right) \left(\log \frac{1}{[\text{H}^+]^4 [\text{SO}_4^{2-}]^2}\right) \\ &= 2.01 - \left(\frac{0.0592}{2}\right) \left(\log \frac{1}{(20)^4 (10)^2}\right) = 2.22 \text{ V} \end{split}$$

$$q = (0.100 \text{ mol Pb}) \left(\frac{2 \text{ mol } \overline{e}}{\text{mol Pb}}\right) \left(\frac{96500 \text{ C}}{\text{mol } \overline{e}}\right)$$
$$= 19300 \text{ C}$$

Energy = 
$$qE = (19300 \text{ C})(2.22 \text{ V}) = 42.8 \text{ kJ}$$

**11.** (c) The reduction potential of lead half-cell is given by

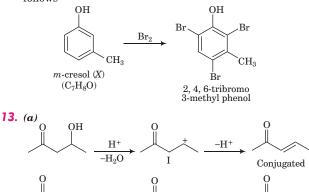
$$E(Pb) = E^{\circ}(Pb) - \left(\frac{0.0592}{2}\right) \left(\log \frac{1}{0.100}\right)$$

= -0.126 - 0.0296 = -0.156 VThe potential of the thallium half-cell is more negative E(Tl) = E(Pb) - 0.443 = -0.156 - 0.443 = -0.599 V For Tl<sup>+</sup> +  $\bar{e} \longrightarrow$ Tl ( $E^{\circ} = 0.336$  V), the concentration of Tl<sup>+</sup> is given by

$$E = E^{\circ} - (0.0592) \left( \log \frac{1}{[\text{Tl}^+]} \right)$$
  
-0.599 = - 0.336 + (0.0592)(log [Tl^+])  
[Tl^+] = 3.6 × 10^{-5}

$$K_{\rm sp} = [{\rm Tl}^+][{\rm Br}^-] = 3.6 \times 10^{-6}$$

**12.** (d) Compound  $X(C_7H_8O)$  is insoluble in aqueous NaHCO<sub>3</sub> but soluble in NaOH, so it is phenol. Since, the number of C-atoms remains the same after bromination, the compound must be *m*-cresol and reactions takes place as follows



Although both reactions are giving the same product, but carbocation I is more stable than II, so I is easily dehydrated.

TΤ

**14.** (a) The mass of  $1.00 \text{ cm}^3 (\text{C}_2\text{H}_5)_4\text{Pb}$  is  $(1.00 \text{ cm}^3) (1.66 \text{ g/cm}^3) = 1.66$ ;

This is the amount needed per litre.

In terms of moles,

ÓН

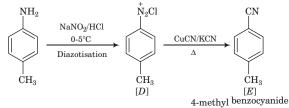
Number of mole of (C  $_{2}$ H  $_{5}$ )  $_{4}$ Pb needed =  $\frac{1.66 \text{ g}}{323 \text{ g}/\text{mol}}$ 

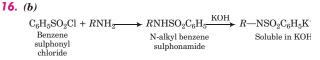
-H-

The chemical equation shows that 1 mole  $(C_2H_5)_4Pb$  requires 4 moles of  $C_2H_5Cl$ . Hence, 4(0.00514) = 0.0206 mole  $C_2H_5Cl$  is needed.

$$m(C_2H_5Cl) = (0.0206 \text{ mol}) (64.5 \text{ g/mol})$$
  
= 1.33 g C <sub>5</sub>H<sub>5</sub>Cl.

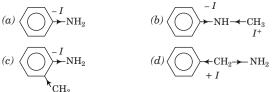






# 🔁 BRAIN TEASERS

**17.** (d) —  $CH_3$  group (an electron releasing (+*I*-effect) (group) increases electron density at N-atom, hence basic nature is increased.



-C<sub>6</sub>H<sub>5</sub> decreases electron density on N-atom, thus, basic nature is decreased. (Lone pair on N in aniline compounds is delocalised alongwith  $\pi$ -electrons in benzene).

18. (c) The reaction of white phosphorus with aqueous alkali is

 $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ In the above reaction, phosphorus is simultaneously oxidised  $(P_4 \longrightarrow NaH_2 PO_2)$  as well as reduced  $(\stackrel{0}{P}_{4}\longrightarrow\stackrel{-3}{P}H_{3}).$ 

Therefore, this is an example of disproportionation reaction. Oxidation number of phosphorus in PH3 is -3 and in NaH<sub>2</sub>PO<sub>2</sub> is +1. However, +1 oxidation number is not given in any option, one might think that NaH<sub>2</sub>PO<sub>2</sub> has gone to further decomposition on heating.

$$2NaH_{2}PO_{2} \xrightarrow{\Delta} Na_{2}HPO_{4} + PH_{2}$$

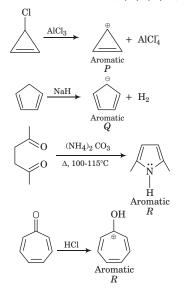
 $H_2\ddot{O}$ 

**19.** (a)  $SiCl_4$  reacts with water due to vacant *d*-orbitals available on Si-atom as shown on right side No such vacant *d*-orbitals are available on C-atom, hence CCl<sub>4</sub> does not react with water.



Otherwise, both  $SiCl_4$  and  $CCl_4$  are covalent.

**20.** (d) A species is said to have aromatic character if (i) ring is planar (ii) there is complete delocalisation of  $\pi$ -electrons (iii) Huckel rule i.e.  $(4n + 2) \pi$ -electrons rule is followed. where, n is the natural number  $(0, 1, 2, 3, \ldots)$ .



	n	$(4n + 2) \pi$ -elect	rons	
P	0	2		
Q	1	6	(including lone pair)	
R	1	6	(including lone pair on $N$ )	
$\boldsymbol{S}$	1	6		
In all cases, there is complete delocalisation of $\pi$ -electrons.				

**21.** (a)  $CH_3 \overline{C}H_2 > \overline{N}H_2 > H - C = \overline{C} > H\overline{O}$ 

It is because the order of acid i.e. strength of their conjugate acid is  $CH_3CH_3 < NH_3 < H - C \equiv C - H < H_2O$ :

**22.** (a) 
$$A_1 \xrightarrow{\text{Calcination}} 2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O}$$

$$\begin{array}{c} A_{1} \longrightarrow \operatorname{CuCl}_{2} + \operatorname{CO}_{2} + \operatorname{H}_{2}\operatorname{O} \\ 2\operatorname{Cucl}_{2} + 4\operatorname{KI} \longrightarrow 2\operatorname{CuI} + \operatorname{I}_{2} + 4\operatorname{KCl} \\ 2\operatorname{Cu}_{2}\operatorname{S} + 3\operatorname{O}_{2} \longrightarrow 2\operatorname{Cu}_{2}\operatorname{O} + 2\operatorname{SO}_{2} \\ \operatorname{Cu}_{2}^{A_{2}} + 2\operatorname{Cu}_{2}\operatorname{O} \stackrel{\Delta}{\longrightarrow} 6\operatorname{Cu} + \operatorname{SO}_{2} \end{array}$$

**23.** (c)  $XeF_6$  on complete hydrolysis produces  $XeO_3 \cdot XeO_3$  on reaction with O H produces HXeO<sub>4</sub> which on further treatment with  $\bar{O}\bar{H}$  undergo slow disproportionation reaction and produces XeO<sub>6</sub><sup>4-</sup> alongwith oxidation half-cell in basic aqueous solution.

 $HXeO_4^- + 5OH \longrightarrow XeO_6^{4-} + 3H_2O + 2e^-$ Reduction half-cell in basic aqueous solution.

 $HXeO_{4}^{-} + 3H_{2}O + 6\overline{e} \longrightarrow Xe + 7OH$ Balanced overall disproportionation reaction is

 $4\mathrm{HXeO}_{4}^{-} + 8\bar{\mathrm{O}}\,\mathrm{H} \longrightarrow \underbrace{3\,\mathrm{XeO}_{6}^{4-} + \mathrm{Xe}}_{6} + 6\,\mathrm{H}_{2}\mathrm{O}$ 

Complete sequence of reaction can be shown as  $XeF_6 + 3H_2O \longrightarrow XeO_3 + 3H_2F_2$ 

$$\xrightarrow{\bar{\mathrm{OH}}} \mathrm{HXeO}_{4}^{-} \xrightarrow{\bar{\mathrm{OH}}/\mathrm{H}_{2}\mathrm{O}} \xrightarrow{} \operatorname{disproportionation}$$

$$XeO_{6}^{4-}(s) + Xe(g) + H_{2}O(l) + O_{2}(g)$$

**24.** (a)  $Zn_2[Fe(CN)_6], K_3[Co(NO_2)_6]$  and

(NH<sub>4</sub>)<sub>3</sub>[As(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>] show colour due to *d*-*d* transition while BaCrO<sub>4</sub> is coloured due to charge transfer phenomenon.

Further, according to spectrochemical series, the strong ligand possessing complex has higher energy and hence, lower wavelength. Therefore, complexes containing NO<sub>2</sub>, NH<sup>+</sup><sub>4</sub>, O<sup>2-</sup> etc., ligands show yellow colour, while CN forces the complex to impart white colour.

25. (a) Rhombic sulphur has a eight membered puckered ring structure. On heating this ring tends to break and linear chained sulphur is formed. When sulphur melts, the S<sub>8</sub> rings slip and roll over one another very easily. It gives rise to a clear mobile liquid.

When liquid sulphur is further heated to higher temperature, rings are broken giving long chain sulphur molecules. This long chain molecules of sulphur gets entangled into one another increasing viscosity of molten sulphur.



# CHEMICAL BONDING FOR CLASS XI

Topicwise Collection of best subjective problems

## Very Short Answer Type [1 Mark]

- **1.** Write the Lewis dot structure of BF<sub>3</sub>.
- **2.** Why  $AIF_3$  is a high melting solid whereas  $SiF_4$  is a gas? [HOTS]
- **3.** Which oxide of nitrogen is isoelectronic to  $CO_2$ ?
- 4. How many  $\sigma$  and  $\pi$ -bonds are present in tetracyanomethane?
- 5. Write the hybridisation of each C-atoms in  $CH_2 = CH CH = CH C \equiv CH$
- **6.** Why ice is more denser than water? [HOTS]

### Very Short Answer Type [2 Marks]

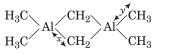
**7.** Predict the number of lone pair of electrons on the central atom of the following molecules.

(a)  $NH_3$  (b)  $H_2O$ 

- All the C—O bonds in carbonate ion (CO<sub>3</sub><sup>2-</sup>) are equal in length. Explain. [NCERT Exemplar]
- 9. Predict all the bond angles in the following molecules.

(i) 
$$CH_3Cl$$
 (ii)  $CH_2$ =CHCl

**10.** In the following molecule, how the bond length '*x*' and '*y*' are related to each other.



[HOTS]

**11.** Draw the geometry of  $ICl_2^-$ .

- **12.** Give reason, why
  - (a)  $O_2$  molecule is paramagnetic?
  - (b) Write down the correct formal charge on the atoms of the

following molecule.



**13.** Give an example of the species that contain three bond pairs and two lone pairs around the central atom.

#### Short Answer Type [3 Marks]

14. Predict the shape of the following molecules on the basis of their hybridisation.

 $BCl_3, CH_4, CO_2, NH_3$  [NCERT Exemplar]

- **15.**  $BF_3$  and graphite, both are  $sp^2$  hybridised.  $BF_3$  is bad conductor and graphite is a good conductor of electricity. Why? [HOTS]
- **16.** Use the molecular orbital energy level diagram to show that  $N_2$  would be expected to have a triple bond.  $F_2$ , a single bond and  $Ne_2$ , no bond. [NCERT Exemplar]
- 17. (a) Although electronegativities of Cl and N-atoms are same but chlorine does not form hydrogen bond. Why?
  - (b)  $\rm NH_3$  can be liquefied more easily than HCl gas, Why?
- **18.** Predict the dipole moment of
  - (i) a molecule of the type  $A\!X_2$  having a linear geometry.
  - (ii) a molecule of the type  $A\!X_4$  having tetrahedral geometry.
  - (iii) a molecule of the type  $A\!X_4$  having square planar geometry.

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# 🔁 TOUCH UP

- **19.** Explain the terms bond length, bond energy and bond angle.
- **20.** Describe hybridisation in the case of  $PCl_5$  and  $SF_6$ . The axial bonds are longer as compared to equatorial bonds in  $PCl_5$ , whereas in  $SF_6$  both axial bonds and equatorial bonds have the same bond length. Explain. [NCERT Exemplar]
- **21.** Write the significance and limitations of octet rule.
- **22.** Arrange the following in the order of decreasing bond angle by giving reason.

#### $NO_2$ , $NO_2^+$ , $NO_2^-$ .

**23.** In both water and dimethyl ether (CH<sub>3</sub>—O—CH<sub>3</sub>), oxygen atom is central atom and has the same hybridisation, yet they have different bond angles,

Which one has greater bond angle? Give reason.

[NCERT Exemplar, HOTS]

- **24.** Explain why carbon has a valency of four not two and why are the four C—H bonds in methane identical ?
- 25. What is an ionic bond? With two suitable examples, write the difference between an ionic and a covalent bond. [NCERT Exemplar]

## Value Based Type [4 Marks]

**26.** Zain, a student of class XI, was very keen to do experiments and of knowledge from them. One day he took some sugar and salt separately and added some acid of sulphur (which is generally used for toilet cleaning) and noticed the changes. He got confused as he know that the reaction of salt should be faster. Next day, he asked about his experiment to his science teacher, who clarified the reason for the result he got.

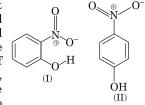
Read the above passage and answer the following questions.

- (i) Can you guess why Zain thought the reaction of salt should be fast?
- (ii) What clarification had been given by the teacher?
- (iii) Draw the electron dot structure of acid of sulphur and salt.
- (iv) What values do you observe in Zain and his teacher? [VBQ]

### Long Answer Type [5 Marks]

- **27.** I. Elements X, Y and Z have 4, 5 and 7 valence electrons, respectively.
  - (a) Write the molecular formula of the compounds formed by these elements individually with hydrogen.
  - (b) Which of these compounds will have the highest dipole moment? [NCERT Exemplar]

- II. Give reason, for the following.
  - (a) Covalent bonds are directional bonds while ionic bonds are non-directional.
  - (b) Water molecule has bent structure, whereas carbon dioxide molecule is linear.
  - (c) Ethyne molecule is linear.
- **28.** (a) Give the example to explain bond pairs and lone pairs of electrons.
  - (b) The H—S—H bond angle in  $H_2S$  is 92.2° whereas the H—O—H bond angle in  $H_2O$  is 104.5°, why?
  - (c) Arrange the following ions in the increasing order of their polarisability  $F^-, Cl^-, Br^-, I^-$
  - (d) Arrange the following molecules in the decreasing order of their dipole moment H<sub>2</sub>O, NF<sub>3</sub>, NH<sub>3</sub>, CH<sub>4</sub>
  - (e) What is the hybridisation and geometry of N-atom in pyridine ?
- **29.** (a) What factors favour the formation of ionic bond? Explain with examples.
  - (b) Arrange the following in the increasing order of ionic character and also give the reason. NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, MgO
  - (c) Predict the geometry of  $XeF_4$  molecule.
  - (d) The experimentally determined N—F bond length in  $NF_3$  is greater than the sum of the single covalent radii of N and F.
  - (e) How many nodal planes are present in  $\pi(2p_x)$  and  $\pi^*(2p_x)$  molecular orbitals?
- **30.** (a) Structures of molecules of two compounds are given below.
  - (i) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding?
  - (ii) The melting point of a compound depends on several other things on the basis of the extent of hydrogen bonding, explain which of the above two



compounds will show higher melting point?

- (iii) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will from hydrogen bond with water easily and be more soluble in it?
- (b) With the help of molecular orbital theory, predict which of the following species is diamagnetic H<sup>+</sup><sub>2</sub>, O<sub>2</sub>, O<sup>2</sup><sub>2</sub><sup>+</sup>?
- (c) Which of the following has highest lattice energy and why?

CsF, CsCl, CsBr, CsI. [NCERT Exemplar]

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# **ALCOHOLS, PHENOLS & ETHERS** FOR CLASS XII

# Topicwise Collection of Best Subjective Problems

## Very Short Answer Type [1 Mark]

- 1. What is denatured alcohol? [NCERT Exemplar]
- 2. Although phenol is an acid, yet it does not react with sodium bicarbonate solution. Why? [HOTS]
- **3.** Of the two hydroxy organic compounds *ROH* and R'OH, the first one is basic and other is acidic in behaviour. How is R different from R'? [Delhi 2013 C]
- **4.** Draw the structure of an organic compound hex-1-en-3-ol.
- 5. Phenyl methyl ether reacts with HI to give phenol and methyl iodide and not iodo benzene and methyl alcohol. Why? [Delhi 2010 C]
- 6. Give the order of dehydration of primary, secondary and tertiary alcohols.
- 7. Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain. [NCERT Exemplar]
- 8. Name the factors responsible for the solubility of alcohols in water. [NCERT Exemplar]
- 9. Write the IUPAC name of the following compounds.

CERT Exemplar]

CH<sub>3</sub>

**10.** Write the mechanism of the following reaction.

 $CH_{3}CH_{9}OH \xrightarrow{HBr} CH_{3}CH_{9}Br + H_{9}O$ [Foreign 2014; Delhi 2014]

# Very Short Answer Type [2 Marks]

- **11.** Use a Grignard's reagent to prepare the following alcohol: 3-methylpentan-3-ol.
- **12.** How will you distinguish between 1-phenyl ethanol and 2-phenyl ethanol?

13. Arrange the following in the decreasing order of their boiling points.  $CH_3$ 

$$CH_2OH$$
,  $HOCH_2CH_2OH$ ,  $CH_3CH_2CI$ 

#### [Delhi 2008; All India 2016]

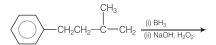
## Short Answer Type [3 Marks]

- **14.** Give any three methods of preparation of alcohols.
- **15.** Draw the structure and name the product formed if the following alcohols are oxidised. Assume that an excess of oxidising agent is used.
  - (i) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (ii) 2-butanol
  - (iii) 2-methyl-1-propanol [Delhi 2012]
- **16.** Account for the following.
  - (i) The boiling point of ethers are lower than isomeric alcohols.
  - (ii) *ortho*-nitrophenol more acidic than is ortho-methoxy phenol.
  - (iii) Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. [Delhi 2011C]
- 17. Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism. [NCERT Exemplar]
- **18.** Why phenol has smaller dipole moment than methanol?

**19.** Give the product of the following reaction.  
(i) 
$$H \to Zn \text{ dust} \to (ii)$$
  $H \to Br_2 \to (iii)$   $H \to Br_2 \to ZTS \to DTS$ 

- **20.** Why is the C—O—H bond angle in alcohols slightly less than the tetrahedral angle, whereas the C—O—C bond angle in ether is slightly greater? [NCERT Exemplar; HOTS]
- **21.** Write steps to carry out the conversion of phenol to aspirin. [NCERT Exemplar]
- 22. The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why? [NCERT Exemplar]
- **23.** Predict the product of the following reaction.

# 🔁 TOUCH UP



- 24. Explain the following with an example for each.
  (i) Kolbe's reaction (ii) Reimer-Tiemann reaction
  (iii) Williamson ether synthesis [All India 2014 C]
- 25. State the products of the following reactions.
   (i) CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub> + HBr →

(ii) 
$$OC_2H_5 + HBr -$$

(iii) 
$$(CH_3)_3C \longrightarrow OC_2H_5 \xrightarrow{HI}$$

[Foreign 2012]

# Value Based Type [4 Marks]

**26.** Anas and Umar are good friends. They sit in the class room side by side but Umar has a bad breath. Anas took him to the dentist. The dentist after examining said that Umar suffers from the dental disease Pyorrhoea. The doctor cleaned his teeth and asked Umar to brush the teeth atleast twice a day and use mouthwash after every meal.

Answer the following questions.

- (i) Name the main constituent of mouth wash.
- (ii) In which solvent, these constituents are dissolved?
- (iii) Give the values of Anas.

# Long Answer Type [5 Marks]

- **27.** Name the reagents used in the following reactions.
  - (a) Dehydration of propan-2-ol to propene.
  - (b) Oxidation of primary alcohol to carboxylic acid
  - (c) Oxidation of primary alcohol to an aldehyde.
  - (d) Butan-2-one to butan -2-ol.
  - (e) Cyclohexanone to 1-ethylcyclohexanol.
- 28. (a) Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why? [NCERT Exemplar]
  - (b) Explain why nucleophilic substitution reactions are not very common in phenols?

#### [NCERT Exemplar, HOTS]

- **29.** An ether  $(A) C_6 H_{14}O$ , when heated with excess of hot conc. HI produced two alkyl halides which on hydrolysis form compounds (*B*) and (*C*). Oxidation of (*B*) gave an acid (*D*) whereas oxidation of (*C*) gave a ketone (*E*). Deduce the structural formulae of (*A*), (*B*), (*C*), (*D*) and (*E*). [HOTS]
- **30.** (a) In Kolbe's reaction, instead of phenol, phenoxide ion is treated with CO<sub>2</sub>. Why?
  - (b) Compare the acidities of  $ClCH_2CH_2OH$  and  $CH_3CH_2OH$ .

#### Solutions of these Questions are Available at our website www.arihantbooks.com

#### Continued from Page 39

- **23.** (a) Both assertion and reason are true and reason is the correct explanation of the assertion.
- **24.** (a)  $PF_5$  is one of the exception of octet rule. In this case an electron from 3s orbital excites and jumps to the 3d-orbital thus making 5 electrons available for sharing and hence, forms the  $PF_5$  molecule.

**25.** (a) The cations of II and IV groups are precipitated as their sulphides. Precipitation of group II cations require low concentration of sulphide so, HCl is added to the original solution before passing  $H_2S$  gas (common ion effect). For IV group cations, large concentration of  $S^{2-}$  is required in order to exceed ionic product than solubility product.

26. (c) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH CH<sub>3</sub>
$$\xrightarrow{C_{2}H_{5}O'K^{+}}_{alc.KOH}$$
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH ==CH<sub>2</sub>  
Br
(A)
  
and
$$\begin{array}{c}H\\H_{5}C_{2}\\CH_{3}\\Cis-2\text{-pentene}\\(B)\end{array}$$

$$\begin{array}{c}H\\H_{5}C_{2}\\CH_{3}\\CH_{3}\\CH_{5}C_{2}\\CH_{3}\\CH_{5}C_{2}\\CH_{3}\\CH_{5}C_{2}\\CH_{5}\\CH_$$

By Saytzeff's rule, substituted alkenes are more stable, hence, B or C is predominant than A. Between *cis* and *trans* isomers, *trans* is more stable. Therefore, C is predominant.

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- **27.** (b) It is true that alcohols are dehydrated to alkenes in the presence of zeolites. This is because zeolites are **shape-selective**, porous solid catalysts.
- (d) Arsenious sulphide is a negative sol. According to Hardy-Schulze rule, coagulating power of an electrolyte is directly proportional to the valency of the active ions. Hence, the coagulating power of different cations for arsenious sulphide sol decreases as

$$Al^{3+} > Ba^{2+} > Na^+$$
.

**29.** (c) 2, 4-dinitrophenyl hydrazine (2, 4-DNP) is also called Brady's reagent. It reacts with carbonyl compounds to form a yellow precipitate.

$$\begin{array}{c} R \\ R \\ \hline \\ R \\ \hline \\ C = O + H_2 N \cdot N H \\ \hline \\ \hline \\ R \\ \hline \\ R \\ \hline \\ \\ R \\ \hline \\ C = N \cdot N H \\ \hline \\ \hline \\ NO_2 \\ \hline \\ NO_2$$

**30.** (d) 1,3-butadiene is the monomer unit of buna-S. For natural rubbers monomer unit is isoprene. The origin of natural rubber are natural resources, thus it is a natural polymer. Natural rubber is prepared from rubber latex (contains 35% rubber) which is a colloidal dispersion of rubber in water and is obtained from rubber trees (*Hevea brasilienses*).

Examples of anionic addition polymerisation is vinylidene cyanide, vinylidene ester, derivatives of acrylonitrile,  $\alpha$ -methylstyrene etc.

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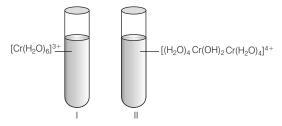
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1. The following two test tubes contains two forms of Cr(II) ion which are shown below.



What are the colours of solutions in test tubes I and II, respectively?

2. Fill in the blanks.

 $\cap$ 

$$^{252}_{98}$$
Cf +  $^{10}_{5}$ B  $\rightarrow$  3  $^{1}_{0}n$  + ...

- 3. Anifreeze consists an aqueous solution of ...
- **4.** CO<sub>2</sub> bubbles out of solution when a carbonated beverage is opened, because the partial pressure of CO<sub>2</sub> above the solution is ...

- 5. Solar panels, made of ..., are used both as an energy source and as arhitectual elements in the buildings.
- 6. List the substances BaCl<sub>2</sub>, H<sub>2</sub>,CO, HF and Ne in the increasing order of boiling points.
- **7**. A teaspoonful of sugar  $(C_{12}H_{22}O_{11})$  is dissolved in a glass of water and a teaspoonful of sugar is dissolved in swimming pool full of water which one has greater number of moles of sugar?
- 8. Usually surroundings contain far more matter than the system and hence have a much greater heat capacity consequently, the temperature of the surroundings often does not change significantly, even though energy transfer has occurred. For evaporation of water at 25°C, how much temperature of surrounding drop?
- 9. A glass sphere containing a few iodine crystals rests on the ground in desert sunshine. The hotter the flask, the more iodine sublimies, producing which colour?
- **10.** How much of energy released on explosion of 1000 tons of dynamite?

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