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N	IATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) 2017-18	
Exa	mination Date : 26-11-2017 Time: 2 Hrs. Max. Marks : 240	
Q.	PAPER CODE : C321 HBCSE Olympiad (STAGE - 1)	
	the question paper code mentioned above on YOUR answer sheet (in the space provided), otherwise your answer sheet will be assessed. Note that the same Q. P. Code appears on each page of the question paper.	
	INSTRUCTION TO CANDIDATES	
1.	Use of mobile phones, smart phones, ip ads during examination is STRICTLY PROHIBITED.	
2.	In addition to this question paper, you are given answer sheet along with Candidate's copy.	
2. 3.	On the answer sheet, fill up all the entries carefully in the space provided, ONLY In BLOCK	
0.	CAPITALS. Use only BLUE or BACK BALL PEN for making entries and marking answer.	
	Incomplete / incorrect / carelessly filled information may disgualify your candidature.	
4.	On the answer sheet, use only BLUE or BLACK BALL POINT PEN for making entries and filling the bubbles.	
5.	The question paper contain 80 multiple-choice question. Each question has 4 options, out of	
0.	which only one is correct. Choose the correct alternative and fill the appropriate bubble, as shown	
	Q. No. 22 (a) 💿 🕜	
6.	A correct answer carries 3 marks and 1 mark will be deducted for each wrong answer.	
7.	Any rough work should be done only in the space provided.	
8.	Periodic Table is provided at the end of the question paper.	
9.	Use of a nonprogrammable calculator is allowed.	
10.	No candidate should leave the examination hall before the completion of the examination.	
11.	After submitting your answer paper, take away the Candidate's copy for your reference.	
	Please DO NOT make any mar other than filling the appropriate bubbles properly in the space provided on the answer sheet. Answer sheet are evaluated using machine, hence CHANGE OF ENTRY IS NOT ALLOWED.	
	Scratching or overwriting may result in wrong score.	
	DO NOT WRITE ANYTHING ON THE BACK OF ANSWER SHEET.	
Read	the following instructions after submitting the answer sheet.	
12.	Comments regarding this question paper, if any, may be filled in Google forms only at <u>https://google/forms/9GP03NRgUVuhWJn52</u> till 28 th November, 2017 .	
13.	The answers/solutions to this question paper will be available on our website — www.iapt.org.in by 2 nd December, 2017.	
14.	Certificates & Awards	
	Following certificates are awarded by the IAPT to students successful in NSEs	
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16.	List of students (with centre number and roll number only) having score above MAS will be displayed on our website (www.iapt.org.in) by 22 nd December, 2017. See the Eligibility Clause in the Student's brochure on our website.	
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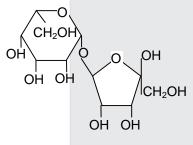
1. At constant T and P, 5.0 L of SO₂ are reacted with 3.0 L of O₂ according to the following equation 2SO₂ (g) + O₂ (g) \rightarrow 2SO₃ (g)

The volume of the reaction mixture at the completion of the reaction is

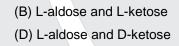
Ans. (C)

 $\begin{array}{cccc} 2SO_2 \left(g\right) + O_2 \left(g\right) \rightarrow 2SO_3 \left(g\right) \\ \text{Sol.} & \text{Initial volume} & 5 \text{ L} & 3 \text{ L} & 0 \\ \text{Volume after} & 0 & + \left(3 - 2.5\right) + 5 & = 5.5 \text{ L} \\ \text{reaction} & & = 0.5 \end{array}$

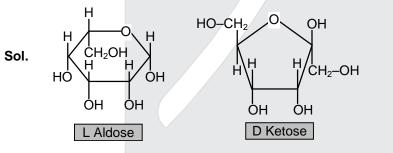
2. The following disaccharide is made up of



- (A) D-aldose and D-ketose
- (C) D-aldose and L-ketose



Ans. (D)



- One mode of 4-nitrocatechol (4-nitro-1,2-dhydroxybenzene) on treatment with an excess of NaH followed by one mole of methyl iodide gives-
 - (A) 4-nitro-1, 2-diamethox ybenzene
 - (C) 2-methox y-5 nitrophenol
- (B) 4-nitro-5methy-1, 2-dimethox ybenzene
- (D) 2-methoxy-4nitrophenol

Ans. (D)



The colour changes of an indicator HIn in acid base titrations is given below

HIn (aq) \implies H⁺ (aq) + In⁻ (aq)

Colour X Colour Y

Which of the following statements is correct?

- (A) In a strong alkaline solution colour Y will be observed
- (B) In a strong acidic solution colour Y will be observed
- (C) Concentration of in $\bar{}$ is higher than that of HIn at the equivalence point
- (D) In a strong alkaline solution colour X is observed

Ans. (A)

- **Sol.** It is an acidic indicator therefore will remain in ionized form in strong alkaline solution (opposite ion effect).
- 5. The table below gives the results of three titrations carried out with 0.200 M HCl to determine the molarity of a given NaOH solution using phenolphthalein as indicator. NaOH was taken in the burette and HCl was taken in a conical flask for the titrations

Titration No.	V HCI(mL)	V _{NaOH (mL)}	M _{NaOH moldm⁻³}
1	21.4	19.3	0.222
11	18.6	16.8	0.221
III	22.2	21.1	0.210

The actual molarity of the prepared NaOH solution was 0.220 mol dm⁻³. Which among the following could be the reason for the wrong value obtained in titration III?

(A) Number of drops of phenolphthalein added to the titration flask was more in this titration

(B) The concentration of HCI was wrongly used as 0.250 M for the calculation of M $_{\rm NaOH}$

(C) A few drops of NaOH solution were spilled outside the titration flask during titration

(D) A few drops of the neutralized solution from titration II were left behind in the flask

Ans. (C)

Sol.

$$[OH^{-}] = \frac{n_{OH^{-}}}{V_{OH^{-}}} = \frac{n_{acid}}{V_{NaOH}} = \frac{[HCI]V_{HCI}}{V_{NaOH}} = 0.21 \text{ M} < 0.220$$

6 The solution with pH value close to 1 is

NaOH

HCI

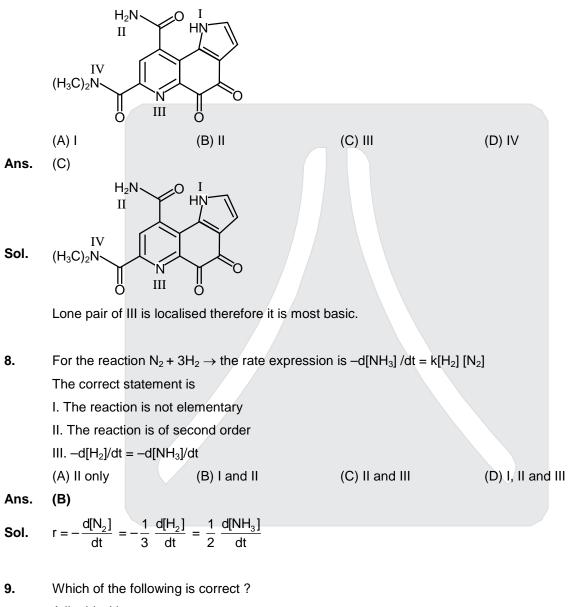
- (A) 10 mL of 0.1 M HCI + 90 mL of 0.1 M NaOH
- (B) 55 mL of 0.1 M HCl + 45 mL of 0.1 M NaOH
- (C) 75 mL of 0.2 M HCl + 25 mL of 0.2 M NaOH
- (D) 75 mL of 0.2 M HCl + 25 mL of 0.1 M NaOH
- Ans. (C)



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Sol.	$[H^{+}] = \frac{10^{-1}}{75 + 25} = 10^{-1} \text{ M}$
	or pH = 1

7. The most basic nitrogen in the following compound is



A liquid with

- (A) low vapour pressure will have a low surface tension and high boiling point
- (B) high vapour pressure will have high intermolecular forces and high boiling point
- (C) low vapour pressure will have high surface tension and high boiling point
- (D) low vapour pressure will have low surface tension and low boiling point $% \left(\mathcal{D}^{\prime}\right) =\left(\mathcal{D}^{\prime}\right) \left(\mathcal{$

Ans. (C)

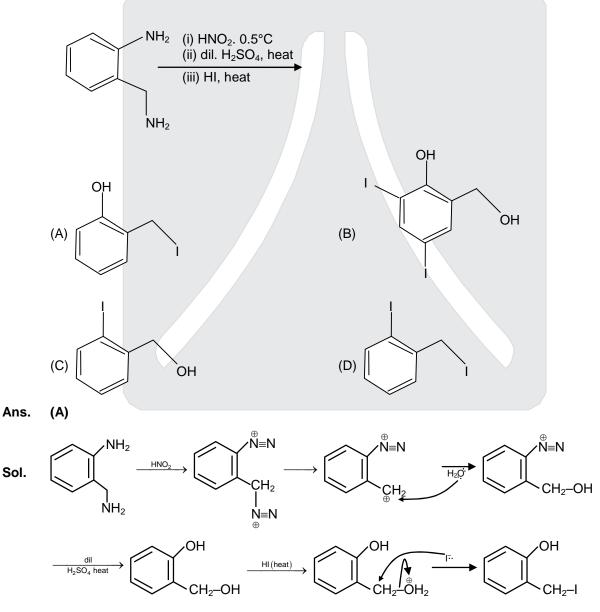
Sol. A liquid with low vapour pressure (less volatile) will have a high surface tension and high boiling point



- At 25°C, nitrogen exists as N_2 and phosphorous exists as P_4 because
- (A) N₂ has valence electrons only in bonding and nonbonding orbitals, while P has valence
- electrons in both bonding and antibonding orbitals
- (B) higher electronegativity of N favours formation of multiple bonds
- (C) bigger size of P does not favour multiple bonds
- (D) P has preference to adapt structures with small bond angles
- Ans. (C)

10.

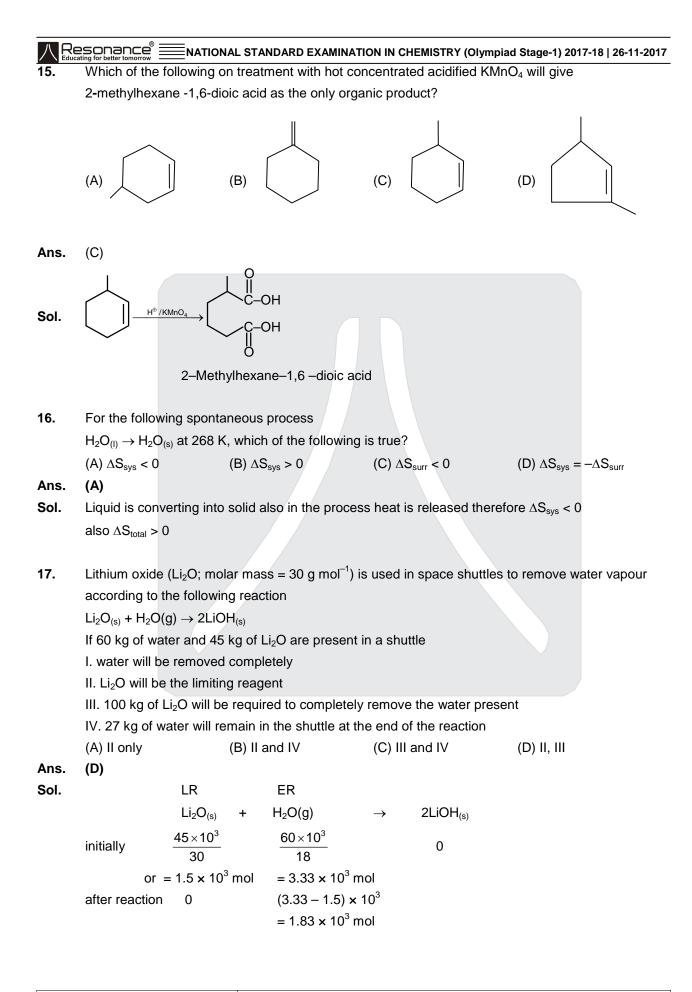
- Sol. Nitrogen forms multiple bonds due to small size.
- 11. The product of the following reaction is

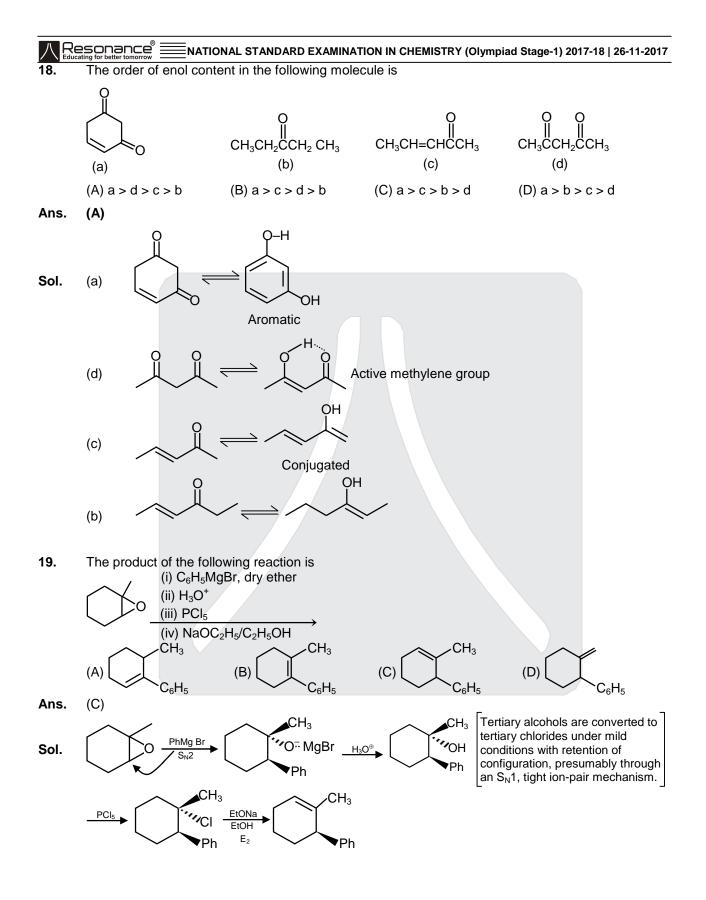




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12.	Three samples of 100 g of water (samples I, II and III), initially kept at 1 atm pressure and 298 K
	were given the following treatments.
	Sample I was heated to 320 K and cooled to 298 K
	Sample II was heated to 300 K, cooled to 273 K and heated to 298 K
	Sample III was heated to 373 K and cooled to 298 K
	At the end of these processes, the internal energy of
	(A) III is the highest
	(B) II is the highest
	(C) I and III are the same, II is lower than that of I and III
	(D) I, II and III are the same
Ans.	(D)
Sol.	Internal energy change is a state function.
4.0	
13.	For the reaction
	$5 \text{ Br}^{-}(\text{aq}) + \text{BrO}_{3}^{-}(\text{aq}) + 6\text{H}^{+}(\text{aq}) \rightarrow 3\text{Br}_{2}(\text{aq}) + 3\text{H}_{2}\text{O}(\text{I})$
	the rate expression was found to be $-d[BrO_3^-] / dt = k [Br^-] [H^+]^2 [BrO_3^-]$
	Which of the following statements is /are correct?
	I. Doubling the initial concentration of all the reactants will increase the reaction rate by a factor of
	8
	II. Unit of rate constant of the reaction in a buffer solution is min ⁻¹
	III. Doubling the concentration of all the reactants at the same time will increase the reaction rate
	by a factor of 16
	IV. rate of conversion of BrO_3^- and rate of formation of Br^- are the same
	(A) I and II (B) II and III (C) II and IV (D) III only
Ans.	(D)
Sol.	$r = -\frac{d[BrO_3^-]}{dt} = \frac{1}{3} \frac{d[Br_2]}{dt}$
	$r' = K[2Br^{-}] [2H^{+}]^{2} [2BrO_{3}^{-}]$
	= 16 r
14.	In the Lewis structure of ozone (O_3) , the formal charge on the central oxygen atom is
	(A) +1 (B) -1 (C) 0 (D) -2
Ans.	(A)
Sol.	+1 -1 _0
501.	0* <u>`</u> 0



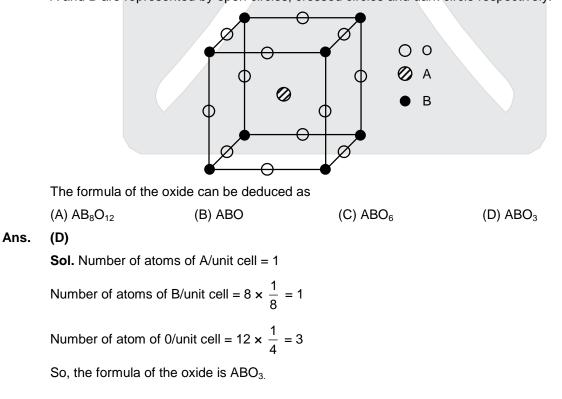


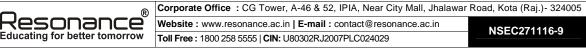




Resonance Mational Standard EXAMINATION IN CHEMISTRY (Olympiad Stage-1) 2017-18 | 26-11-2017 At constant volume, 6.0 mol of H₂ gas at 0°C and 100 kPa was heated to 250 kPa. The molar heat of H₂ at constant pressure (C_P) = 28.9 J mol⁻¹. (assume that the heat capacity values do not change with temperature). The final temperature of the H₂ gas and the change in entropy of the process are (A) 273°C and 113 kJ mol⁻¹ K⁻¹ (B) 410°C and 158.8 J mol⁻¹ K⁻¹ (C) 682.5°C and 113 J mol⁻¹ K⁻¹ (D) 682.5 K and 113 J mol⁻¹ K⁻¹ (D) Ans. $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ Sol. $\frac{100}{273} = \frac{250}{T_2}$ or $T_2 = 682.5$ K $\Delta S = nC_V \ln \frac{T_2}{T_1}$ = 2.303 n(C_P - R) log $\frac{T_2}{T_1}$ $= 2.303 \times 6 \times (28.9 - 8.314) \log \frac{682.5}{273}$ \approx 113 J mol⁻¹ mol⁻¹

21. The cubic unit cell of an oxide of metals A and B is as given below, in which oxygen. A and B are represented by open circles, crossed circles and dark circle respectively.

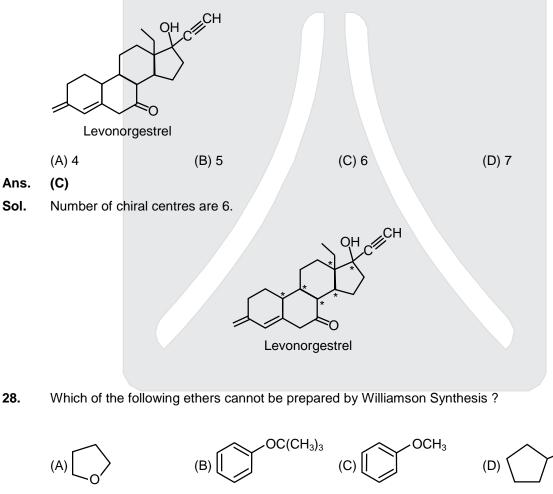




22.	esonance Mational Standard EXAMINATION IN CHEMISTRY (Olympiad Stage-1) 2017-18 26-11-201 When a medal is electroplated with silver (Ag)			
	(A) The medal is the anode			
	(B) Ag metal is the cathode			
	(C) The solution contains Ag ⁺ ions			
	(D) The reaction at the anode is $Ag^+ + e^- \longrightarrow Ag$			
Ans.	(C)			
Sol.	For electroplating of metal with silver			
	Cathode \rightarrow Metal			
	Anode \rightarrow Ag			
	Solution \rightarrow Electrolyte containing Ag ⁺			
23.	The energy of an electron in Bohr's orbit of hydrogen atom is -13.6eV. The total electronic energy			
	of a hypothetical' He atom is which there are no electron- electron repulsions is			
	(A) 27.2 eV (B) -27.2 eV (C) -108.8 eV (D) 108.eV			
Ans.	(C)			
Sol.	Electronic energy per electron = $-13.6 \times 4 \text{ eV}$			
	Total Electronic energy = $-13.6 \times 4 \times 2 = -108.8 \text{ eV}$			
24.	lodine is a solid and sublimes at ordinary temperature. This is because of :			
	(A) weak I-I bonds			
	(B) strong I-I bonds			
	(C) lone pair-bond pair repulsions			
	(D) weak van der Waals forces between I_2 molecules			
Ans.	(D)			
Sol.	I_2 is solid & sublimes at ordinary temperature because of weak vander waal's force between I_2			
	molecules.			
25.	The equilibrium constant of the following isomerisation reaction at 400K and 298 K are 2.07 and			
	3.42 respectively.			
	cis-butene $\underset{k_{-1}}{\overset{k_1}{\underset{k_{-1}}{\longrightarrow}}}$ trans-butene			
	Which of the following is/are correct ?			
	I. The reaction is exothermic			
	II. The reaction is endothermic			
	III. At 400K 50% of cis-butene and 50% of trans-butene are present of equilibrium			
	IV. Both at 298K and 400K, $k_1 = k_{-1}$			
	(A) I and IV (B) II and IV (C) I and III (D) I only			
Ans.	(D)			
Sol.	As on T increase, K_{eq} is increasing, Reaction is exothermic.			
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26.	26. Which of the following will not give a straight line plot for an ideal gas ?				
	(A) V vs T	(B) T vs P	(C) V vs I/P	(D) V vs I/T	
Ans.	(D)				
Sol.	PV = nRT				
	$V = \frac{nRT}{P}$				
	V v/s $\frac{1}{T}$ will not b	be a straight line.			

27. Levonorgestrel is a commonly used contraceptive. The number of chiral centres present in this molecule is :



Ans. (B)

Sol. $PhO^{-} + (CH_3)_3C \longrightarrow X \longrightarrow No Reaction$

Or $(CH_3)_3CO^- + Ph - X \longrightarrow No$ Reaction

Hint : $(CH_3)_3C$ —X and Ph—X do not react by SN² reaction.

- **29.** IUPAC name of complex ion $[CrCl_2(ox)_2]^{3-}$ is
 - (A) dichlorodioxalatochromium (III)
- (B) dioxalatodichlorochromate(III)

OCH₃

- (C) dichlorodioxalatochromate(III)
- (D) bisoxalaeodichlorochromate(III)

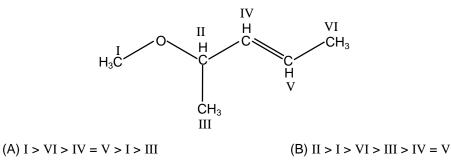


Ans.	(C)		
Sol.	IUPAC name is dichlorodioxalatochromate (III)		
30.	Sodium azide (NaN ₃) is used in airbag of cars. This is safety device with inflates on an impact		
	according to the reaction $2NaN_3 \rightarrow 2Na + 3N_2$		
	An air bag of a particular car can be filled with 44.8 L of gas at STP. The mass (g) of ${\sf NaN}_3$		
	required to fill this airbag completely at 298K and 1 atm. pressure is :		
Ans.	(A) 87 (B) 130 (C) 84 (D) 100 (A)		
Sol.	As the maximum volume of airbag will remain same irrespective of temperature hence to fill me bag at 298 K. V = 44.8 L T = 298 K P = 1 atm n (of N ₂) = 1.83		
	moles of NaN ₃ required = $\frac{2}{3} \times 1.83 = 1.22$ mole		
	mass of NaN ₃ required = 1.22 × 65 = 79.4 g \Rightarrow So it should be bonus. Comment : If we consider that airbag will contain same mole at both temperature (273 K & 298 K) (i.e. assuming volume expansion at bag with temperature) So moles of N ₂ at STP = 2 (T = 273 K) Moles of N ₂ at 298 K & 1 atm = 2 Moles of NaN ₃ reqd. = $\frac{2}{3} \times 2 = \frac{4}{3}$		
	Mass of NaN ₃ required = $\frac{4}{3} \times 65 \approx 84$ g.		
	So (A) can be considered with the above unjustified assumptions.		
31.	Which of the following mixtures of water and H_2SO_4 would have mass percentage of H_2SO_4 close to 30? (A) 30 g $H_2SO_4 + 100$ g H_2O (B) 1 mol of $H_2SO_4 + 2$ mol of H_2O (C) 1 mol of $H_2SO_4 + 200g$ of H_2O (D) 0.30 mol $H_2SO_4 + 0.70$ mol H_2O		
Ans.	(C)		
Sol.	Mass percentage of $H_2SO_4 = \frac{98}{298} \times 100 = 32.88$		
	Closest to 30.		
32.	In chlorides, the common oxidation states of aluminium and thallium are +3 and +1 respectively because. (A) TI-CI bond is ionic and AI-CI bond is covalent (B) 6s electrons of TI are bound more strongly than the 3s electron of AI (C) TI-CI bond is stronger than AI-CI bond (D) a electrons of Alexes hand here always then the Calestonne of TI		

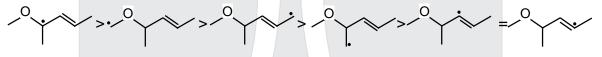
- (D) 3s electrons of AI are bond strongly than the 6s electrons of TI
- Ans.
- (B) Sol. 6s electrones of TI are bond more strongly than 3s electrons of AI. (inert pair effect) Also Ionisation energy of TI > Ionisation energy of AI.



33. In the given compound the order of case with which hydrogen atom can be abstracted from carbons I to VI is :



- (C) II > I > III > VI > IV = V (D) IV > II > I > III > IV = V
- Ans. (B)
- **Sol.** Breaking of C–H bond is inversely related to stability of intermediate free radical.



(Stability order of free radical)

Use the table given below to answer questions 34 and 35

Reaction		E ₀ /V
$Ag \rightarrow Ag^+$	+ e ⁻	-0.80
Cr ³⁺ + 3e ⁻	\rightarrow 3Cr	-0.74
Zn ²⁺ + 2e ⁻	\rightarrow Zn	-0.76
I ₂ (s) + 2e ⁻	→ 2 I ⁻	0.54
Co ²⁺ + 2e ⁻	→ Co	-0.28
Ni ²⁺ + 2e ⁻	→ Ni	-0.26

(B) -0.02V

34. The best reducing agent among the following is

(A)
$$Ag^+$$
 (B) Zn^{2+} (C) Cr^{3+} (D) I^-

- Ans. (D)
- **Sol.** Ag⁺, Zn²⁺, Cr³⁺ are not reducing agents. I⁻ Is a reducing agent.

35. E^o of the given cell is :

NI (Ni⁺²,1.0M) (Co⁺²,1.0M) Co

(A) +0.02V

Ans. (B)

Sol.

$$\begin{split} \mathsf{E}^{\mathsf{o}}_{\mathsf{cell}} &= \mathsf{E}^{\mathsf{o}}_{\mathsf{cathode}\,(\mathsf{RP})} - \mathsf{E}^{\mathsf{o}}_{\mathsf{anode}(\mathsf{RP})} \\ &= \mathsf{E}^{\mathsf{o}}\mathsf{Co}^{+2}/\mathsf{Co} - \mathsf{E}^{\mathsf{o}}\mathsf{Ni}^{+2}/\mathsf{Ni} \end{split}$$

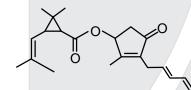
= -0.28 - (-0.26) = -0.02 V

(D) +0.54V

(C) -0.54V

NATIONAL STANDARD EXAMINATION IN CHEMISTRY (Olympiad Stage-1) 2017-18 | 26-11-2017 36. Which of the following is not a pair of a Lewis acid and a Lewis base ? (A) H^+ , $(C_2H_5)_2O$ (B) H_2O , AlCl₃ (C) Fe^{3+} , CO (D) SiF₄, BF₃

- Ans. (D)
- **Sol.** Both $SiF_4 \& BF_3$ are both lewis acids.
- **37.** The type of isomerism that $Co(NH_3)_4Br_2CI$ can exhibit is/are
 - (A) geometric and ionisation
 - (B) ionisation
 - (C) Optical and ionisation
 - (D) Optical, ionisation and geometric
- Ans. (A)
- Sol. It can exhibit geometric & ionisation.
- 38. Pyrethrins are produced in chrysanthemum flowers and used as insecticides.
 Structure of pyrethrin I is given below

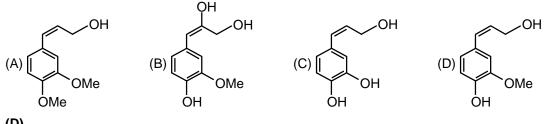


Pyrethrin I (molar mass = 32.8g/mol)

The volume of 0.05 mol dm³ bromine water that would with 500 mg sample of Pyrethrin I is

(A) 12.2 cm^3 (B) 122 dm^3 (C) 122 cm^3 (D) $1.31 \times 10^3 \text{ cm}^3$

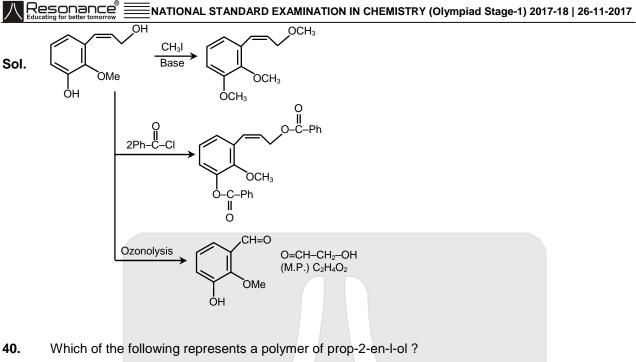
- Ans. (C)
- Sol. Total position where Bromine water can attack is four.
- **39.** Coniferyl alcohol is isolated from pine trees. The following observations were made about this alcohol.
 - I. It forms methylated product with Mel in presence of base
 - II. One equivalent of coniferyl alcohol reacts with two equivalents of benzoyl chloride
 - III. Upon ozonolysis, coniferyl alcohol gives a product 'Y' (M.F $C_2H_4O_2$).



Ans. (D)



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Ans. (B)

Sol.

$$nCH_2=CH \xrightarrow{Polymerisation} CH_2-CH \xrightarrow{CH_2-CH}_n$$

41. A 500 mL glass flask is filled at 298 K and 1 atm, pressure with three diatomic gases X, Y and Z. The initial volume ratio of the gases before mixing was 5:3:1. The density of the heaviest gas in the mixture is not more than 25 times that of the lightest gas. When the mixture was heated, vigorous reactions take place between X and Y and X and Z in which all the three gases were completely used up.

The gases X, Y, Z respectively are (A) H_2 , O_2 , N_2 (B) H_2 , O_2 , Cl_2 (C) H_2 , F_2 , O_2 (D) O_2 , H_2 , F_2

Ans. (C)

Sol. According to given data.

Mole ratio of gas x,y,z are 5 : 3 : 1

 \rightarrow As given in the question that the density of heaviest gas in the mixture is not more then 25 times that of lightest gas. Hence gas mix should be H₂, F₂, O₂

$$\rightarrow x = H_2, \qquad y = F_2, \qquad z = O_2$$

$$H_2 + F_2 \longrightarrow 2HF \qquad H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

$$5a \quad 3a \quad - \qquad 2a \quad a \qquad 2a$$

$$2a \quad - \quad 6a \qquad - \quad - \qquad 2a$$

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42. The reaction X + Y → Z is first oder with respect to X and second order with respect to Y. The initial rate of formation of Z = R mol dm³ sec⁻¹ when [X]₀ and [Y]₀ are 0.40 mol dm⁻³ and 0. mol dm³ respectively. If [X]₀ is halved and [Y]₀ is doubled, the value of the initial rate would become
(A) 4R
(B) R/4
(C) R
(D) 2R

Sol. $X + Y \longrightarrow Z$ $(Rate)_1 = K[X] [Y]^2$ $(Rate)_2 = K[\frac{X}{2}] [2Y]^2$ $\frac{(Rate)_1}{(Rate)_2} = \frac{1}{2}$ $(Rate)_2 = 2(Rate)_1 = 2R$

43. Which one of the following statements is not correct about glucose ?

(molar mass of glucose = 180 g mol^{-1})

(A) An aqueous 0.25 M solution of glucose is prepared by dissolving 45 g of glucose in water to give 1000 cm³ of solution

- (B) 1.00 mmol glucose has a mass of 180 mg
- (C) 90.0 g glucose contain 1.8×10^{22} atoms of carbon
- (D) 100 cm³ of a 0.10 M solution contains 18 g of glucose

Ans. (C) & (D)

- **Sol.** (A) W _{glucose} = $0.25 \times 10 \times 180 = 45$ g
 - (B) $W_{glucose} = 1 \text{ mmole} \times 180 = 180 \text{ mg}$

(C) No. of C-atoms = $\frac{90}{180} \times N_A \times 6 = 18 \times 10^{23}$

(D) $W_{glucose} = 100 \times 0.1 \times 10^{-3} \times 180 = 1.8 \text{ g}$

Hence C & D both are in correct

44. The van der Waals equation for one mole of a real gas can be written as

 $(P + a/V^2)$ (V - b) = RT. For the gases H₂, NH₃, and CH₄, the value of 'a' (bar L⁻² mol⁻²) are 0.2453, 4.170 and 2.253 respectively.

Which of the following can be inferred from the 'a' values ?

- (A) NH₃ can be most easily liquified
- (B) H₂ can be most easily liquified
- (C) value of 'a' for CH₄ is less than that of NH₃ because it has the lower molar mass
- (D) intermolecular forces are the strongest in hydrogen
- Ans. (A)
- **Sol.** van der Wall's constant 'a' gives information about force of attraction between gaseous molecules. Higher the value of 'a' higher will be force of attraction, and easier the liquefaction of gas. Order of intermolecular force of attraction = $H_2 < CH_4 < NH_3$



45. Terpinen-4-ol is an active ingredient in tea tree oil has the following structure



The correct observations for terpinen-4-ol is/are

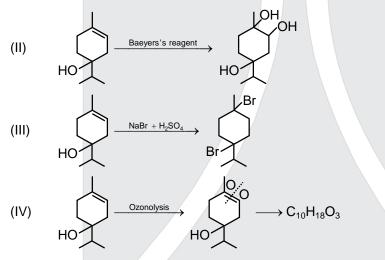
I. It rotates the plane of plane polarized light.

- II. It reacts with Baeyer's reagent to form form a triol
- III. On reaction with NaBr and H_2SO_4 , it gives form a diobromo compound
- IV. On ozonolysis it gives a compound with molecular formula $C_{10}H_{18}O_3$
- (A) I, II, III and IV (B) I, III and IV (C) II and III (D) III and IV

Ans. (A)

Sol.

(I) Terpinen-4-ol is an optically active molecule because it is chiral molecule



46. The correct order of the ability of the leaving group is

(A) $OCOC_2H_5 > OC_2H_5 > OSO_2Et > OSO_2CF_3$

(B) $OC_2H_5 > OCOC_2H_5 > OSO_2CF_3 > OSO_2Me$

- (C) $OSO_2CF_3 > OSO_2Me > OCOC_2H_5 > OC_2H_5$
- (D) $OCOC_2H_5 > OSO_3CF_3 > OC_2H_5 > OSO_2Me$
- Ans. (C)
- Sol. Weaker bases are better leaving group.

 $\downarrow \text{ order of } \mathsf{K}_{\mathsf{b}}: \ddot{\mathbf{O}}\mathsf{SO}_2\mathsf{CF}_3 > \ddot{\mathbf{O}}\mathsf{SO}_2\mathsf{Me} \ > \ \ddot{\mathbf{O}}\mathsf{COC}_2\mathsf{H}_5 > \ \ddot{\mathbf{O}}\mathsf{C}_2\mathsf{H}_5$



47.

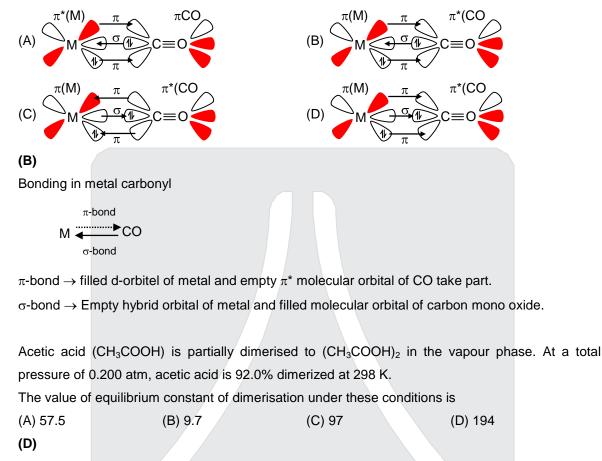
Ans.

Sol.

48.

Ans.

Metal 'M' forms a carbonly compound in which it is present in its lower valance state. Which of the following bonding is possible in this metal carbonyl ?



Sol.
$$2CH_{3}COOH \longrightarrow (CH_{3}COOH)_{2}$$

 $a \longrightarrow (CH_{3}COOH)_{2}$
 $a - 0.92a \qquad 0.46 a$
 $0.08 a \qquad 0.46 a$
 $Kp = \frac{\frac{0.46a}{0.54a} \times 0.02}{\left(\frac{0.08a}{0.54a} \times 0.02\right)^{2}} \simeq 194.$

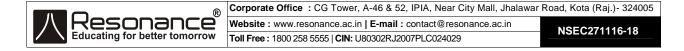
49. Silanes are silicon hydrides of general formula Si_nH_{2n+2} and have several applications. From the data given below, the bond dissociation enthalpy of Si-Si bond can be deduced as

 $\Delta H \text{ of the reaction } 2Si(s) + 3H_2(g) \longrightarrow Si_2H_6(g) \text{ is } 80.3 \text{ kJ mol}^{-1}$ Bond dissociation enthalpy for H – H = 436 kJ/mol Bond dissociation enthalpy for Si – H = 304 kJ/mol $\Delta f_H [Si(g)] 450 \text{ kJ mol}^{-1}$

(B) 384.3 kJ mol⁻¹

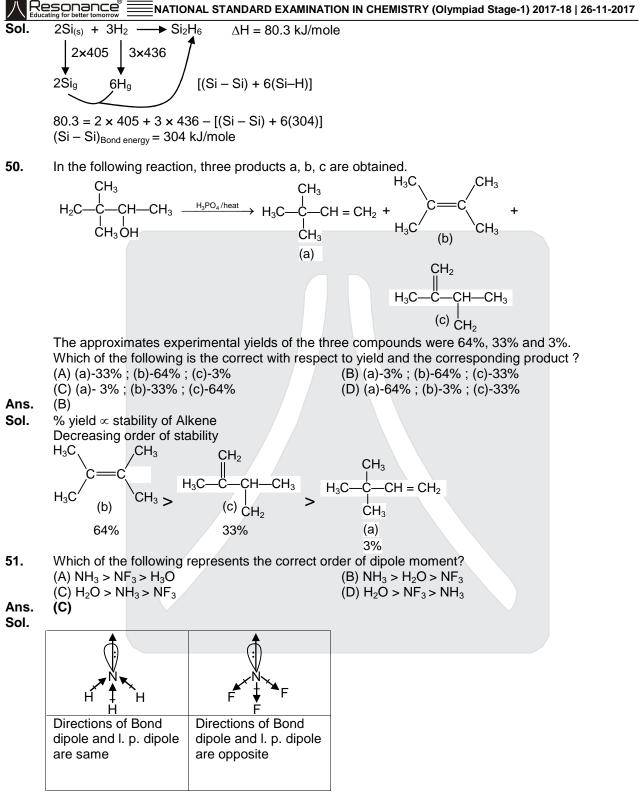
Ans. BONUS

(A) - 304 kJ mol-1



(C) 304 kJ mol⁻¹

(D) – 384.3 kJ mol⁻¹

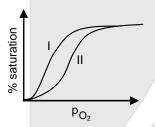


Hence $H_2O > NH_3 > NF_3$





- The best reaction sequence for the synthesis of 2-pentanone would be -
- (A) $CH_{3}CH_{2}CH_{2}CHO \xrightarrow{CH_{3}MgI/ether} X \xrightarrow{H^{*},H_{2}O}$ (B) $CH_{3}CH_{2}CH_{2}CN \xrightarrow{CH_{3}MgI/ether} X \xrightarrow{H^{*},H_{2}O}$ (C) $CH_{3}CH_{2}CH_{2}CHO \xrightarrow{CH_{3}MgI/ether} X \xrightarrow{H^{*},H_{2}O}$ (D) $CH_{3}CH_{2}CH_{2}MgI + CH_{2}O \xrightarrow{ether} X \xrightarrow{H^{*},H_{2}O}$ Ans. (B) Sol. $CH_{3}CH_{2}CH_{2}CN \xrightarrow{CH_{3}MgI/Ether} CH_{3}-CH_{2}-CH_{2}-C=NMgI \xrightarrow{H^{\oplus},H_{2}O} CH_{3}-CH_{2}-CH_{2}-C-CH_{3}$ $\xrightarrow{CH_{3}} MH_{3} \xrightarrow{+} MH_{3}$ $\xrightarrow{H^{*}}Mg(OH)I$
- **53.** Haemoglobin is a Fe containing protein responsible for oxygen transport in the blood. The curves given below indicate the percentage saturation of haemoglobin by O_2 as a function of partial pressure of O_2 .



Which of the following statement/s is /are correct for the given curves?

I. In presence of CO_2 , higher P_{O_2} is needed for a given percentage saturation

II. In presence of CO₂, lower P_{O_2} is needed for a given percentage saturation

III. The maximum percentage saturation is not affected by the presence of CO₂

IV. In the absence of CO₂, maximum saturation of haemoglobin occurs at lower p_{O_2}

Ans. (C)

Sol. According to given information graph I would be in presence of CO₂ and II would be in absence of CO₂.

Now we can conclude from graph that

- (i) In presence of CO_2 higher P_{O_2} in needed for a given percentage saturation.
- (ii) The maximum percentage saturation is not affected by presence of CO₂.
- (ii) In the absence of CO_2 , maximum saturation of haemoglobin occurs at lower P_{O_2} .



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- 4. An appropriate reagent for the conversion of 1-propanol to 1-propanal is
 - (A) acidified potassium dichromate
 - (B) alkaline potassium permanganate
 - (C) pyridinium chlorochromate
 - (D) acidified CrO₃

Ans. (C)

- **Sol.** Mild oxidising agent pyridinium chlorochromate (PCC) will oxidise primary alcohol into aldehyde.
- 55. A student performed an experiment to determine the molecular formula of a given sample of hydrated copper(II) sulphate by weighing the sample before and after heating. The formula obtained experimentally was CuSO₄.5H₂O while the actual formula of the given sample is CuSO₄. 5H₂O. Which experimental error would account for the wrongly obtained result ?
 - (A) During heating, some of the hydrated copper(II) sulphate was lost
 - (B) The hydrated sample was not heated long enough to remove all the water present
 - (C) Weight of the hydrated sample recorded was less than the actual weight taken
 - (D) The balance used in the study showed all weights consistently high by 0.10g.

Ans. (A)

Sol.
$$W_i = m(ini) = m(CuSO_4 \cdot x H_2O)$$

 $w_f = m(final) = m(CuSO_4) *(possibly dehydrated)$
 $m_{water} = W_i - W_f$
 $n_{water} = \frac{W_i - W_f}{18}$
 $n_{CuSO_4} = \frac{W_f}{M_{CuSO_4}}$
 $x = \frac{n_w}{n_{CuSO_4}} = \frac{W_i - W_f}{18} \times \frac{M_{CuSO_4}}{W_f}$
 $x \propto \left(\frac{W_i}{W_f} - 1\right)$

Correct value of x is 5

Experimental value of x is 5.5

Now, Option (A) is absurd, since $CuSO_4$ cannot evaprate.

(C) is wrong If W_i is less than correct value X_{experi} should be < 5.

$$X_{exp} = \frac{W_i^{correct} + 0.1}{W_f^{correct} + 0.1}$$



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 $\begin{array}{l} \ddots & \displaystyle \frac{W_i^{correct}}{W_f^{correct}} > 1 \quad \ \ ; \ \ adding \ \ same \ no \ to \ numerator \ \ \& \ \ denominator \ \ will \ \ decrease \ the \ fraction. \\ \mbox{Now, look at (B)} \\ W_i = m(CuSO_4.xH_2O) \\ W_f = m(CuSO_4.yH_2O) \ ; \ \ y < x \end{array}$

 $W_{f} = In(CuSO_{4}, yn_{2}O), \quad y < x$ Mass of water evaporated = $W_{i} - W_{f}$ Moles of water evaporated = $\frac{W_{i} - W_{f}}{18}$ $x = \frac{n_{w}}{n_{CuSO_{4}}} = \frac{M_{CuSO_{4}}}{18} \times \frac{W_{i} - W_{f}}{W_{f}} \longleftarrow Since \text{ we (wrongly)}$

 $x = \frac{n_{w}}{n_{CuSO_{4}}} = \frac{M_{CuSO_{4}}}{18} \times \frac{W_{i} - W_{f}^{'}}{W_{f}^{'}} \longleftarrow$ Since we (wrongly) believe it to be anhydrous. $x \propto \left(\frac{W_{i}}{W_{f}^{'}} - 1\right)$

If some water of crystallization is left, W_f must be < W_f (the correct value).

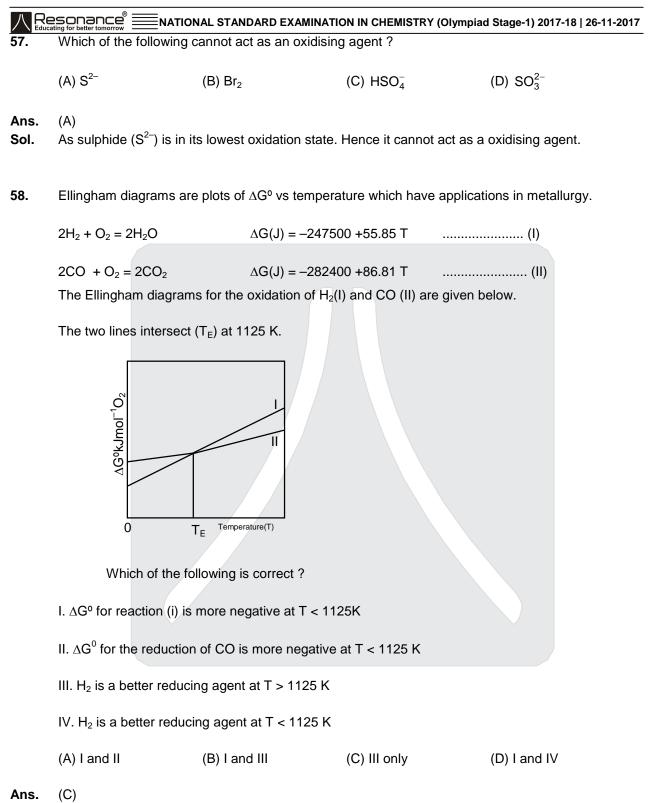
Thus, the incorrect value must be < 5. But it is claimed as 5.5.

Hence, none of the options (A), (B), (C) or (D) are correct. In true spirit of chemical science, this question is ought to be a bonus. However if we assume spillage/any other loss (A) may be taken as the answer.

56. Malic acid is a dicarboxylic acid present in apples and it has the following structure

Which of the following synthetic routes will give (±) malic acid ?





Sol. According to the given data, Plot I is for CO as it has more negative ΔG value Plot II is for H₂. And as we know in the Ellingham diagram, compound for which, the Plot lies below acts as a better reducing agent. So, at T > 1125 K, H₂ is a better reducing agent.

Note: The given graph in the question is not according to given data in the question.



9. Hydrazine used in rocket fuels can be obtained by the reaction of ammonia and hydrogen peroxide according to the following equations

 $2NH_3(g) + H_2O_2(I) \longrightarrow N_2H_4(I) + 2H_2O(I) (\Delta H^{0}_{reaction} = -241 kJ/mol)$ If ΔH^{0} (formation) of NH₃, H₂O₂ and H₂O are -46.1, -187.8 and -285.8 kJ/mol respectively, ΔH^{0} for the decomposition of hydrazine into N₂ and H₂ is

(A) 50.6 kJ/mol (B) 241 kJ/mol (C) -50.6 kJ/mol (D) 120.5 kJ/mol

Ans. (C)

Sol. $2NH_{3(g)} + H_2O_{2(\ell)} \longrightarrow N_2H_{4(\ell)} + 2H_2O_{(\ell)}$

$$\begin{split} &\Delta_{\text{reaction}}^{\circ} = \left(\Delta H_{\text{fN}_2\text{H}_4}^{\circ} + 2x \ \Delta H_{\text{f}}^{\circ}\text{H}_2\text{O}\right) - \left(2x\Delta H_{\text{f}(\text{NH}_3)}^{\circ} + \Delta_{\text{f}(\text{H}_2\text{O}_2)}^{\circ}\right) \\ &- 241 = \ \Delta H_{\text{f}}^{\circ}\left(\text{N}_2\text{H}_2\right) + 2x\left(-285.8\right) - 2x \ (-46.1) + 187.8 \\ &\Delta H_{\text{f}}^{\circ}\left(\text{N}_2\text{H}_2\right) = -241 + 2 \times 285.8 - 2 \times 46.1 - 187.8 \\ &\Rightarrow \qquad \Delta H_{\text{f}(\text{N}_2\text{H}_2)}^{\circ} = 50.6 \text{ kJ / mol.} \end{split}$$

Therefore, for the decomposition of hydrazine into N_2 & H_2 is –50.6 kJ/mol.

60. Sn²⁺ compounds like SnO and SnCl₂ are well known reducing agents, while PbO₂ acts as an oxidizing agent. Which of the following statements support these reactivities?

I. SnO is more stable than ${\rm SnO}_2$

II. Sn⁴⁺ is more stable than Sn²⁺

III. Pb^{4+} is more stable than Pb^{2+}

IV. Pb^{2+} is more stable than Pb^{4+}

(A) I and III (B) I, III and IV

(C) II and IV

(D) I, II and IV

Ans. (C)

Sol. $\operatorname{Sno}^{+2} \longrightarrow \operatorname{Sno}_{2}^{+4} \xrightarrow{Pb} O_{2} \longrightarrow \operatorname{Pb}^{+2} O_{2}$ $\overset{+2}{\operatorname{Sn}} \operatorname{Cl}_{2} \longrightarrow \operatorname{Sn}^{+4} \operatorname{Sn}^{+4} \operatorname{Cl}_{4}$

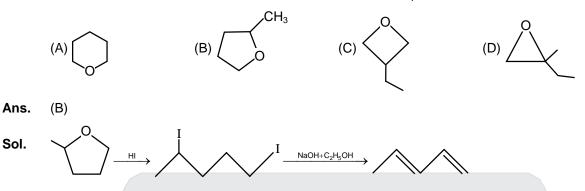
 Sn^{+4} is more stable than Sn^{+2} & Pb^{+2} is more stable than Pb^{+4} . So, Sn^{+2} acts as reducing agents & Pb^{+4} acts as oxidising agents. Above fact can also be explain by inert pair effect.

A fuel/ oxidant system consisting of N,N-dimethylhydrazine (CH₃)₂NNH₂ and N₂O₄ (both liquids) is used in space vehicle propulsion. The liquid components are mixed stichiometrically so that N₂, CO₂ and H₂O are the only products. If all gases are under the same reaction conditions, number of moles of gases produced from 1 mole of (CH₃)₂NNH₂ is

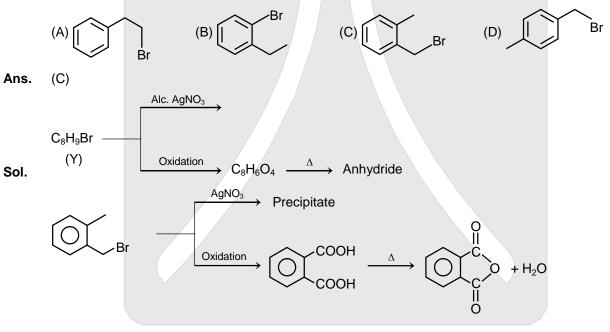
Ans. (C)



62. An ether (X) with molecular formula $C_5H_{10}O$ reacts with excess of hot aq. HI to give a product which on further reaction with hot NaOH in ethanol forms 1,3 pentadiene. Structure of X is



63. Compound 'Y' with molecular formula C₈H₉Br gives a precipitate on heating with alcoholic AgNO₃.
 Oxidation of 'Y' gives products 'Z' (C₈H₆O₄) which gives an anhydride upon heating.
 Compound 'Y' is



64. The observed effective magnetic moment of two octahedral complexes,

 $K_4[Mn(CN)_6].3H_2O(X)$ and $K_4[Mn(SCN)_6]$ (Y) are 2.18 BM and 6.06 BM, respectively. Which of the following is correct?

- I. X is low spin complex with two unpaired electrons
- II. Y is high spin complex with 5 unpaired electrons
- III. X is a high spin complex with two unpaired electrons

(B) I, II

IV. Y is a low spin complex with 5 unpaired electrons

(A) I and III

(C) I, II and IV

(D) I, II and III

Ans. Bonus

Sol. $K_4[Mn(CN)_6].3H_2O \Rightarrow Mn^{2+}$ with CN = 6 & SFL

 \therefore Pairing will take place $(t_{2q}^{221}e_{q}^{00})$



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 \Rightarrow Low spin complex with one unpaired electron.

 $K_4[Mn(SCN)_6] \Longrightarrow Mn^{2+}$ with CN = 6 & WFL

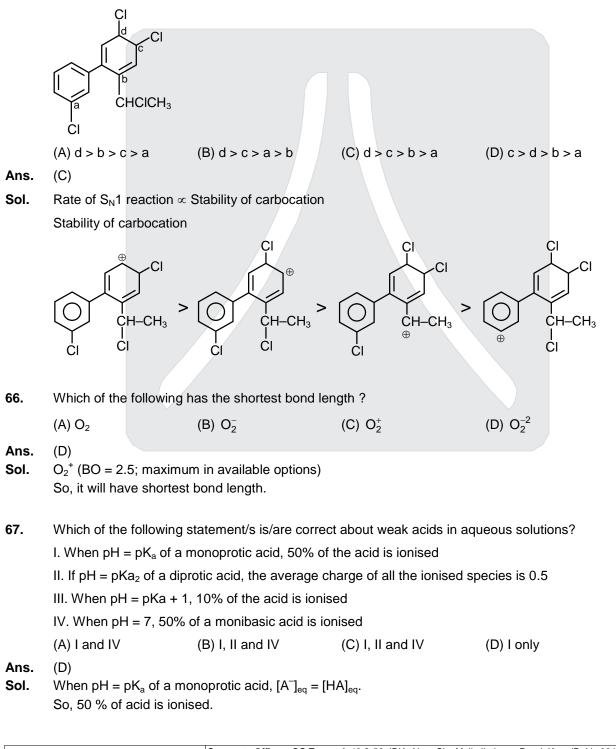
 \therefore Pairing will not take place $(t_{2g}^{111}e_g^{11})$

 \Rightarrow High spin complex with five unpaired electrons.

So, only II statements is correct, which matches with none of given options. So, question should be BONUS.

However, from the available options, (B) seem best.

65. The increasing reactivity of the sites (a-d) in the following compound is $S_N 1$ reaction is





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68.	'lodine number' is the grams of iodine atoms (atomic mass = 127 g mol ⁻¹) that can react completely
	with 100 g of a vegetable oil. Iodine monochloride (ICI) is a reagent used to determine iodine
	number. In an experiment, 25.00 cm^3 of 0.100 mol dm^{-3} ICI was added to 127g of the oil. The
	unreacted ICI was found to be equivalent to 40.00 cm ³ of 0.10 mol dm ⁻³ of $Na_2S_2O_3$.
	The iodine number of the oil can be deduced as
	(A) 127 (B) 100 (C) 200 (D) 50
Ans.	Bonus
Sol.	I-Cl used = 25 mL × 0.1 M = 2.5 mmol
	meq of I-CI left = meq of hypo reacted
	$= 40 \text{ mL} \times 0.1 \text{N}$
	= 4 meq
	mmol of I-Cl left = $\frac{4}{2}$ = 2 mmol
	Thus, mmol of I-CI reacted with 127g vegetable oil = $2.5 - 2 = 0.5$ mmol
	Thus, mmol of ICI with 100g of oil = 0.5 mmol × $\frac{100}{127}$
	Now, each mol of I-CI contains 127 g of Iodine atoms.
	Thus, mass of iodine atom that combines from I-CI on vegetable oil = $\frac{50}{127}$ × 127 mg = 50 mg. =
	0.05g
Note:	(i) There seems to be an error in the printed paper.
	I-CI will add across C = C as follows :
	$ C = C \left(+ I - CI \longrightarrow I - \frac{I}{C} - \frac{I}{C} - CI \right) $
	As per the 'definition' offered in the paper, '50' may be the answer. However, going by the correct
	standard definition of iodine number : instead of 1 mol of I-Cl, 1 mol of I_2 can be added. Thus,
	iodine number will be 100. Final verdict : 68 : Bonus
	Assuming the error of 10^3 is neglected,
	(B) should be the answer (by standard definition).
	(D) may be offered as answer, if the definition given in paper is taken as such.
Comm	
	It is a potentially good but improperly worded question.
69.	When NiO is doped with a small quantity of Li_2O
	(A) both cation and anion vacancies are generated
	(B) Shottky defects are generated
	(C) NiO becomes an n-type semiconductor
	(D) NiO becomes a p-type semiconductor
Ans.	(D)
Sol.	When NiO is doped with a small quantity of Li_2O , a Ni^{2+} can be expected to be replaced by $2Li^+$. A decrease in unpaired electrons would make NiO a p-type semiconductor.

When a sample of gas kept at 20°C and 4.0 atm is heated to 40°C at constant volume

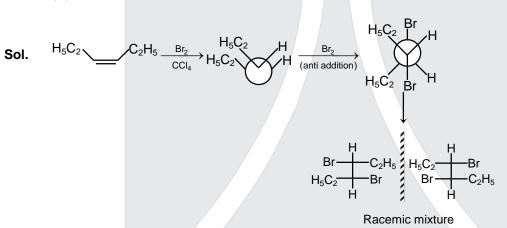
- (A) average speed of the gas molecules will decrease.
- (B) number of collisions between the gas molecules per second will remain the same.
- (C) average kinetic energy of the gas will increase.
- (D) pressure of the gas will become 8 atm.

Ans. (C)

Sol.
$$KE_{avg.} = \frac{f}{2}nRT$$

As T \uparrow , KE_{avg. \uparrow}

- 71. Addition of bromine to cis-3-hexene gives(A) racemic dibromide(B) a mixture of diastereomeric dibromides
 - (C) optically active dibromide
 - (D) meso dibromide
- Ans. (A)



72. An organic compound "X" forms an orange-yellow precipitate with 2,4-DNP reagent. It does not react with aqueous [Ag(NH₃)₂] NO₃. X on reduction with NaBH₄ gives a secondary alcohol and on oxidation with nitric acid yields a dicarboxylic acid containing the same number of carbon atoms. On bromination, X gives a monobromo product. On the basis of these reactions, it can be concluded that X

 contains aldeh 	ydic carbonyl group.		
II. contains ketor	ic carbonyl group.		
III. contains este	r carbonyl group.		
IV. does not cont	ain C=C bonds.		
(A) I only	(B) III and IV	(C) III only	(D) II and IV
(D)			

Ans.

Sol. An organic compounds 'X' forms and orange yellow precipitate with 2, 4-DNP reagent but does not react with aqueous $[Ag(NH_3)_2] NO_3$ confirms presence of C=O group in form of ketone.

'X' on reduction with NaBH₄ gives secondary alcohol again suggests presence of ketone.

'X' on bromination gives mono bromo product which suggests absence of $C=C \le C$ bond because in presence of $C=C \le C$ dibromo product would have been formed.



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B. The undissociated form of a weak organic acid HA can be extracted from the aqueous phase into

an organic phase using a water-immiscible organic solvent according to the following scheme

HA Organic phase

$$K_{D}$$
 Aqueous phase

Which of the following is/are correct for this extraction?

I. [HA]_{org}/[HA]_{aq} depends on the pH of the aqueous phase

II. HA can be efficiently extracted from basic aqueous solutions

III. [HA]_{org}/[HA]_{aq} depends on the initial concentration of HA

IV. $[HA]_{org}/[HA]_{aq} + [A^-]$ depends on the pH of the aqueous phase

(A) II and IV (B) IV only (C) I only (D) III and IV (B) Sol. Even if HA reacts / dissociates in any medium ;

Thus, I and III are wrong.

Now, consider (II). Adding more base will pull the aqueous equilibrium towards right side. Thus, organic HA will be pulled towards aqueous phase. Hence, its extraction by organic phase will be hampered.

Thus (ii) is wrong.

Obviously, only (iv) remains as the correct option. Hence (B) is the answer.

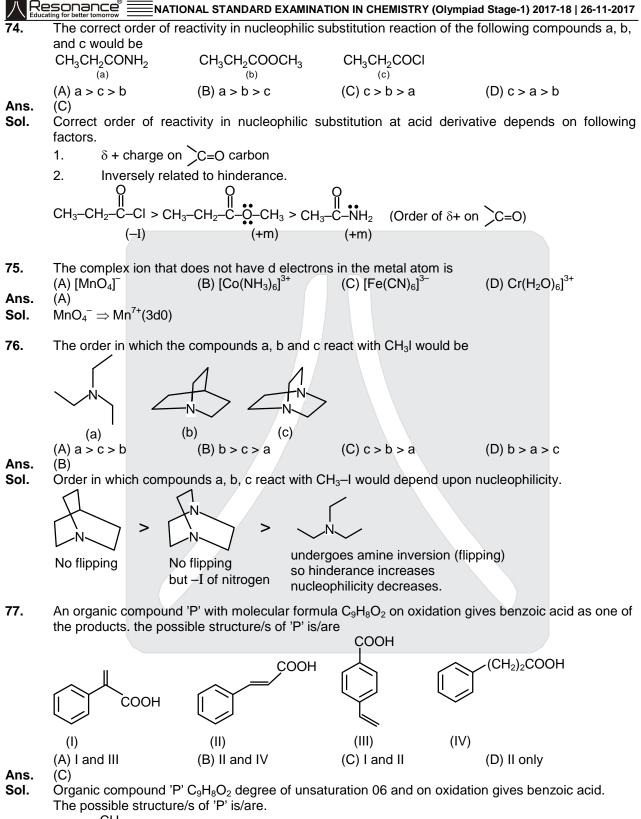
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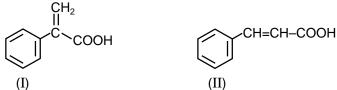
Ans.

Dividing (i) by (ii) :

$$\frac{\left[\mathsf{HA}\right]_{\mathsf{ORG}}}{\left[\mathsf{A}^{-}\right] + \left[\mathsf{HA}\right]_{\mathsf{aq}}} = \frac{\mathsf{K}_{\mathsf{D}}\left[\mathsf{H}^{+}\right]}{\mathsf{K}_{\mathsf{a}} + \left[\mathsf{H}^{+}\right]} = \mathsf{function of pH}.$$









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The energy of an electron in the ground state of H atom is -13 6eV.

The negative sign indicates that

- (A) electrons are negatively charged.
- (B) H atom is more stable than a free electron.
- (C) energy of the electron in the H atom is lower than that of a free electron.
- (D) work must be done to make a H atom from a free electron and proton.

(C) Ans.

- The negative sign in energy of an electron indicates that energy of the electron in the H-atom is Sol. lower than that of a free electron.
- Radius of Ar atom is 145 pm. The percentage volume occupied by an Ar atom at STP is 79.

(A) 0.03 (B) 3.0 (C) 0.30 (D) 0.06
Ans. (A)
Sol.
$$\% = \frac{\frac{4}{3} \times \frac{22}{7} \times (1.45 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{22400} \times 100$$

 $= 0.034$
 ≈ 0.03

80. The reduction of O₂ to H₂O in acidic solution has a standard reduction potential of 1.23 V. If the pH of the acid solution is increased by one unit, half cell potential will

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

- (A) decrease by 59 mV
- (B) increase by 59 mv
- (C) decrease by 236 mV
- (D) increase by 236 mV

Ans. (A)

Sol.
$$E = E^{\circ} - \frac{0.059}{n} \log_{10} Q_{pc}$$
 (at 25°C)

$$E_{i} = 1.23 - \frac{0.059}{4} \log_{10} \frac{1}{(10^{-x})^{4}}$$

$$E_{f} = 1.23 - \frac{0.059}{4} \log_{10} \frac{1}{(10^{-x-1})^{4}}$$
$$E_{f} - E_{i} = 0.059 \log_{10} \left(\frac{10^{-x-1}}{(10^{-x})}\right) = -0.059 \text{ V}$$

: E decreases by 59 mV



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