Maximum Marks: 300

#### **INSTRUCTIONS**

 The question-cum-answer booklet has 40 pages and has 44 questions. Please ensure that the copy of the question-cum-answer booklet you have received contains all the questions.

Write your Roll Number, Name and the name of the Test Centre in the appropriate space provided on the right side.

Write the answers to the objective questions against each Question No. in the Answer Table for Objective Questions, provided on Page No.
 Do not write anything else on this page.

4. Each objective question has 4 choices for its answer: (A), (B), (C) and (D). Only ONE of them is the correct answer. There will be negative marking for wrong answers to objective questions. The following marking scheme for objective questions shall be used:

(a) For each correct answer, you will be awarded 3 (Three) marks.

(b) For each wrong answer, you will be awarded -1 (Negative one) mark.

(c) Multiple answers to a question will be treated as a wrong answer.

(d) For each un-attempted question, you will be awarded 0 (Zero) mark.

(e) Negative marks for objective part will be carried over to total marks.

5. Answer subjective questions only in the space provided after each question.

6. Do not write more than one answer for the same question. In case you attempt a subjective question more than once, please cancel the answer(s) you consider wrong. Otherwise, the answer appearing last only will be evaluated.

 All answers must be written in blue/black/blueblack ink only. Sketch pen, pencil or ink of any other colour should not be used.

 All rough work should be done in the space provided and scored out finally.

No supplementary sheets will be provided to the candidates.

 Clip board, log tables, slide rule, calculator, cellular phone, pager and electronic gadgets in any form are NOT allowed.

11. The question-cum-answer booklet must be returned in its entirety to the invigilator before leaving the examination hall. Do not remove any page from this booklet.

12. Refer to useful data on the reverse.

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# READ INSTRUCTIONS ON THE LEFT SIDE OF THIS PAGE CAREFULLY

	ROL	L NUN	BER	
Name:				
Test Centre	:			

Do not write your Roll Number or Name anywhere else in this questioncum-answer booklet.

I have read all the instructions and shall abide by them.

Signature of the Candidate

I have verified the information filled by the Candidate above.

Signature of the Invigilator

#### Useful Data

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08 \times 10^{-3} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ 

 $N_{\rm A} = 6.02 \times 10^{23}$ 

 $k_{\rm B} = 1.38 \times 10^{-23} \, {\rm J \, K^{-1}}$ 

 $h = 6.6 \times 10^{-34} \, \mathrm{J s}$ 

 $c = 3 \times 10^8 \,\mathrm{m \, s^{-1}}$ 

 $F = 96500 \text{ C mol}^{-1}$ 

 $C_p = 4.2 \text{ J K}^{-1} \text{ g}^{-1}$  for water

(2.303RT)/F = 0.059 V at 298 K

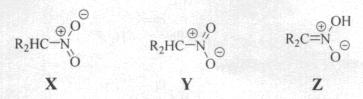
Density of ice and water at 0°C and 1 atm are 0.9 g/cc and 1.0 g/cc, respectively.

 $\ln(1/3) = -1.1$ ;  $\ln(1/2) = -0.69$ ;  $\ln(2/3) = -0.41$ ;  $\ln 2 = 0.69$ 

DO NOT WRITE ON THIS PAGE

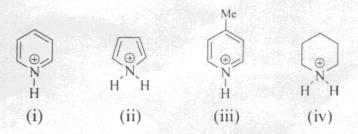
#### IMPORTANT NOTE FOR CANDIDATES

- Questions 1-30 (objective questions) carry <u>three</u> marks each and questions 31-44 (subjective questions) carry <u>fifteen</u> marks each.
- Write the answers to the objective questions in the <u>Answer Table for Objective Questions</u> provided on page 9 only.
- Q.1 The correct statement describing the relationship between



is

- (A) X and Y are resonance structures and Z is a tautomer
- (B) X and Y are tautomers and Z is a resonance structure
- (C) X, Y, and Z are all resonance structures
- (D) X, Y and Z are all tautomers
- Q.2 Among the following, the correct statement concerning the optical activity is
  - (A) a molecule containing two or more chiral centres is always optically active
  - (B) a molecule containing just one chiral centre is always optically active
  - (C) a molecule possessing alternating axis of symmetry is optically active
  - (D) an optically active molecule should have at least one chiral centre
- Q.3 The correct order of acidity among



is

(B) (iv) 
$$<$$
 (iii)  $<$  (i)  $<$  (ii)

$$(C)$$
 (ii) < (i) < (iii) < (iv)

(D) (ii) 
$$<$$
 (iv)  $<$  (i)  $<$  (iii)

Q.4 The major product obtained in the following reaction

(iii)  $\Delta$ 

is

$$\begin{array}{c} \text{(A)} \\ \text{H}_3\text{C} \\ \text{Ph} \end{array} \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array}$$

(B)

$$H_3C$$
 $H_3C$ 
 $CH_3$ 

(D) 
$$Ph$$
  $CH_2$ 

Q.5 The major product of the following reaction

$$H_3C$$
 $H_3C$ 
 $C$ 

anhyd. AICl<sub>3</sub>

is

(A)

(C)

(D)

Q.6 The major product obtained in the following reaction

$$OH$$
  $OH$   $K_2CO_3$   $PhCH_2Br$ 

is

- $(A) \qquad (B) \qquad (O) \qquad (B) \qquad (C) \qquad (C)$
- Q.7 R-(-)-2-Bromooctane on treatment with aqueous KOH mainly gives 2-octanol that is
  - (A) optically active with 'R' configuration
  - (B) optically active with 'S' configuration
  - (C) a racemic mixture
  - (D) a meso compound

Q.8 The major product obtained in the following reaction

is

$$(A) \bigoplus_{O} \bigoplus_{N \text{OMe}} H$$

(C) an equimolar mixture of

OMe

Q.9 The major product obtained in the following reaction

is

Q.10 The products of the following reaction

are

Q.11 When one mole of ice is converted to water at 0°C and 1 atm, the work done (L atm) is

- (A)  $1.1 \times 10^{-4}$
- (B)  $2.0 \times 10^{-3}$
- (C)  $2.0 \times 10^{-4}$
- (D)  $1.1 \times 10^{-5}$

Q.12 When 100 g of water is reversibly heated from  $50^{\circ}\text{C}$  to  $75^{\circ}\text{C}$  at 1 atm, the change in entropy (J K<sup>-1</sup>) of the universe is

- (A) -0.31
- (B) 0.31
- (C) 0
- (D) 3.1

Q.13 For a zero order reaction, units of the rate constant is expressed as

- (A)  $M^{1}s^{-1}$
- (B)  $M^0 s^{-1}$
- (C)  $M^{-1} s^{-1}$
- (D)  $M^0 s^0$

Q.14	$1\times10^{-6}$ moles of the enzyme carbonic anhydrase dehydrates $H_2CO_3$ to produce 0.6 mol of $CO_2$ per second. The turnover number of the enzyme is						
	(A) $N_A \times 6 \times 10^{-5}$ (C) $(6 \times 10^5)/N_A$	\$ 2000 000 de	(B) $(1/6) \times 10^{-5}$ (D) $6 \times 10^{5}$				
Q.15		most probable speed der the same conditions i		000 m s <sup>-1</sup> , the mean/average			
	(A) 1224	(B) 1128	(C) 886	(D) 816			
Q.16	If the electrons were spin 3/2 particles, instead of spin 1/2, then the number of electrons that can be accommodated in a level are						
	(A) 2	(B) 3	(C) 4	(D) 5			
Q.17	For a particle in are	a cubic box, the total no	umber of quantum num	bers needed to specify its state			
	(A) 1	(B) 2	(C) 3	(D) 9			
Q.18	The maximum n	umber of phases that ca	n co-exist in equilibrium	m for a one component system			
	(A) 1	(B) 2	(C) 3	(D) 4			
Q.19	With increasing	pressure, the temperatur	e range over which the l	iquid state is stable,			
	(A) decreases (B) increases (C) remains cons (D) decreases til	stant I the critical pressure and	d then increases				
Q.20	The conductance	e at infinite dilution follo	ows the order				
	(A) $Li^+ > Na^+ >$ (C) $K^+ > Li^+ >$	K <sup>†</sup> Na <sup>†</sup>	(B) $Na^{+} > Li^{+} > (D) K^{+} > Na^{+} > (D) K^{+} > Na^{+} > (D) K^{+} > $	K <sup>†</sup> Li <sup>†</sup>			
Q.21	The V-shape of	SO <sub>2</sub> is due to the present	ce of				

Q.22	The correct order	The correct order of the mean bond energies in the binary hydrides is					
	(A) $CH_4 > NH_3 > H_2O > HF$ (C) $HF > H_2O > CH_4 > NH_3$		(B) $NH_3 > CH_4 > H_2O > HF$ (D) $HF > H_2O > NH_3 > CH_4$				
Q.23	In CsCl structure, Cs <sup>+</sup> ion is	the number of Cs <sup>+</sup> ior	ns that occupy second near	rest neighbour locations of	2		
	(A) 6	(B) 8	(C) 10	(D) 12			
Q.24	In the process						
	<sup>234</sup> <sub>92</sub> U	<sup>230</sup> <sub>90</sub> Th + X	1150 Television (1997)				
	<b>X</b> is  (A) $\alpha$ particle (C) $\beta^+$ emission		(B) β particle (D) γ emission				
Q.25	For tetrahedral confield stabilization of	mplexes, which always energy) is	exhibit high spin states,	the maximum CFSE (crysta	ıl		
	(A) -8 Dq	(B) –12 Dq	(C) –16 Dq	(D) -20 Dq			
Q.26	The most abundan	t element in earth's cru	st is				
	(A) aluminium	(B) iron	(C) silicon	(D) oxygen			
Q.27	Metal-carbon mult frequency of	tiple bonds in metal ca	arbonyls are preferably id	entified from the stretching	3		
	(A) carbon–oxygen bond (C) metal–oxygen bond		(B) metal–carbon bond (D) carbon–carbon bond				
2.28	In general, magnet	ic moment of paramagi	netic complexes varies wit	h temperature as			
	(A) T <sup>2</sup>	(B) T	(C) T <sup>-2</sup>	(D) T <sup>-1</sup>			
).29	The compound have	ring an S–S single bond	l is				
	(A) H <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	(B) H <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	(C) H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	(D) H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>			
).30	In a reaction, Na <sub>2</sub> s reaction is (mol. wt		$Na_2S_4O_6$ . The equivalent	weight of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> for this			
	(A) M	· (B) M/4	(C) M/2	(D) M/3			

## Answer Table for Objective Questions

Write the Code of your chosen answer only in the 'Answer' column against each Question No. Do not write anything else on this page.

Question No.	Answer	Do not write in this column	Question No.	Answer	Do not write in this column
01			16		
02			17		
03			18		
04			19		
05			20		
06			21		
07			22	7.	
80			23		
09			24		
10			25		
11			26		
12			27		
13			28		
14			29		
15			30		

### FOR EVALUATION ONLY

No. of Correct Answers	Marks	(+)
No. of Incorrect Answers	Marks	(-)
Total Marks in Quest	( )	

Q.31 (a) Identify A, B and C in the following reaction sequence.

(b) Identify  $\mathbf{D}$  in the following reaction and suggest a suitable mechanism for its formation.

Me 
$$H_2N-OH$$
  $D$   $(C_7H_9N)$   $EtOH$   $O$ 



Q.32 (a) Explain with the help of mechanisms, the observed stereoselectivity in the following epoxide formation reactions.

(b) Explain on the basis of conformational analysis why (1R,2S)-1,2-dimethyl-cyclohexane is optically inactive at room temperature. (6)

Q.33 (a) Identify E, F and G in the following synthetic transformation.

Me 
$$\frac{Br_2/AcOH}{MeOH}$$
 E  $\frac{NaBH_4}{MeOH}$  F  $\frac{(i) G}{(ii) H^+}$  (9)

(b) An optically active compound **H** (C<sub>5</sub>H<sub>6</sub>O) on treatment with H<sub>2</sub> in the presence of Lindlar's catalyst gave a compound **I** (C<sub>5</sub>H<sub>8</sub>O). Upon hydrogenation with H<sub>2</sub> and Pd/C, compound **H** gave **J** (C<sub>5</sub>H<sub>12</sub>O). Both **I** and **J** were found to be optically inactive. Identify **H**, **I** and **J**. (6)





(9)

- Q.34 (a) A disaccharide **K** gives a silver mirror with Tollen's reagent. Treatment of **K** with MeOH/HCl gives a monomethyl derivative **L**, which does not react with Tollen's reagent. Methylation of **K** with Me<sub>2</sub>SO<sub>4</sub> and NaOH affords an octamethyl derivative of **K**, which upon acidic hydrolysis gives a 1:1 mixture of 2,3,4,6-tetra-O-methyl-D-glucose and 2,3,4-tri-O-methyl-D-glucose. Disaccharide **K** is also hydrolysed by the enzyme maltase. Identify **K** and **L** with proper stereochemistry.
  - (b) Identify  $\mathbf{M}$  and  $\mathbf{N}$  in the following reaction sequence.

$$(i) O_3 \longrightarrow M \xrightarrow{\text{cat. KCN}} N$$
(ii) Zn/AcOH (6)

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Q.35 In the following reaction sequence, identify P, R and S. Suggest suitable mechanisms for the conversion of  $P \rightarrow Q$  and  $R \rightarrow S$ .

$$\begin{array}{c|cccc}
\mathbf{P} & \xrightarrow{\text{(i) } (\text{CH}_3\text{CO})_2\text{O} \\ \text{CH}_3\text{COONa} \\ \text{(ii) } \text{H}^+ & & & & & & \\
\hline
\mathbf{Q} & & & & & \\
\end{array}
\begin{array}{c|cccc}
\mathbf{R} & \xrightarrow{\text{(i) } \text{SOCl}_2} & \mathbf{S} \\
\hline
\mathbf{Q} & & & & \\
\end{array}$$
(15)

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Q.36 (a) Consider the reactions

(I) 
$$Cr_2O_7^{2-}$$
 +  $H_2O_2$   $\xrightarrow{A}$   $CrO(O_2)_2$  room temp.  $Cr^{3+}$  unstable

(II) 
$$Cr^{3+} + H_2O_2 \xrightarrow{B} CrO_4^{2-}$$

- (i) Identify A and B.
- (ii) What is the role of H<sub>2</sub>O<sub>2</sub> in (I) and how does A favour the formation of Cr<sup>3+</sup>?
- (iii) What is the role of  $H_2O_2$  in (II) and how does **B** favour the formation  $CrO_4^{2-}$ ? (9)
- (b) With the help of equations, illustrate the role of a *cis*-1,2-diol in the titration of boric acid with sodium hydroxide. (6)

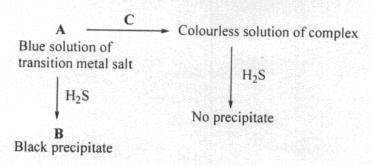




- Q.37 (a) Draw the structure of anionic Ca(II)-EDTA chelate. How many rings are formed in the chelate and specify the number of atoms in each ring? (9)
  - (b) Based on VSEPR theory draw the most stable structure of CIF<sub>3</sub> and XeF<sub>4</sub>. (6)

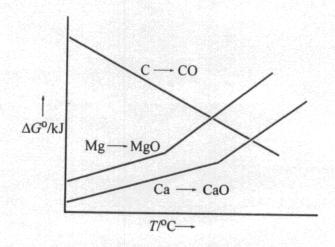
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Q.38 (a) Identify A, B and C in the following reaction scheme



(9)

(b) From the Ellingham diagram given below, identify the metal oxide that can be reduced at a lower temperature by carbon. Justify.



(6)

		ü			
	Λ	N			
	$\vdash$	•	i.		
- 4	L.		L.		

- Q.39 (a) For the complexes [FeF<sub>6</sub>] <sup>3-</sup> and [Fe(CN)<sub>6</sub>] <sup>3-</sup>.

  (i) show the hybridization using VB (valence bond) theory

  (ii) calculate the CFSE (crystal field stabilization energy)

  (9)
  - (b) Identify the dark blue complex formed when [Fe(CN)<sub>6</sub>] <sup>3-</sup> is treated with FeSO<sub>4</sub> and account for the origin of its colour. (6)

Q.40 (a) Consider the equilibrium

$$\mathbf{A}\left(g\right) \longrightarrow \mathbf{B}\left(g\right) + \mathbf{C}\left(g\right)$$

At a constant pressure of 1 atm, **A** dissociates to the extent of 50% at 500 K. Calculate  $\Delta G^{\circ}$  (kJ mol<sup>-1</sup>) for the reaction.

(b) Consider the following redox system

$$Q + 2H^{+} + 2e^{-} \longrightarrow QH_{2}$$
  $E^{0} = 0.699 \text{ V}$ 

Calculate the pH of the solution at 298 K, if the redox potential of the system is 0.817 V.





- Q.41 (a) A stream of oxygen molecules at 500 K exits from a pin-hole in an oven and strikes a slit that selects the molecules travelling in a specific direction. Given that the pressure outside the oven is  $2.5 \times 10^{-7}$  atm, estimate the maximum distance at which the slit must be placed from the pin-hole, in order to produce a collimated beam of oxygen. (Radius of  $O_2 = 1.8 \times 10^{-10}$  m)
  - (b) Liquid water is to be circulated to transfer heat from a source to a sink at 1 atm. Considering this arrangement as a Carnot engine, calculate the maximum theoretical efficiency that can be expected from the system.



- Q.42 (a) Using Heisenberg's uncertainty principle, derive an expression for the approximate ground state energy of a particle of mass m in a one dimensional box of length L. (9)
  - (b) The rate of a chemical reaction doubles when the temperature is changed from 300 K to 310 K. Calculate the activation energy (kJ mol<sup>-1</sup>) for the reaction.



#### Q.43 (a) Consider the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
  $\Delta H^{\circ} = -606.9 \text{ kJ mol}^{-1}$ 

Assuming ideal behaviour, calculate  $\Delta U^{\circ}$  when 1 mol of CH<sub>4</sub> is completely oxidized at STP. (9)

(b) A photochemical reaction was carried out using a monochromatic radiation (490 nm) of intensity 100 W. When the sample was irradiated for 30 min, 0.3 mol of the reactant was decomposed. Estimate the quantum efficiency assuming 50% absorption.
(6)

 $\mathbf{A}$ 



(9)

Q.44 (a) Given that

$$C_{\rm p} - C_{\rm v} = \frac{\alpha^2 T V}{\kappa_{\rm T}}$$
 where  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{\rm p}$  and  $\kappa_{\rm T} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{\rm T}$ 

for a pure substance, show that  $C_p - C_v = R$  for 1 mol of an ideal gas.

(b) Find the eigenvalues of the following 3 × 3 matrix given that 2 is one of the eigenvalues. Compute the determinant of the matrix using the eigenvalues.

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -2 \\ 1 & -1 & 1 \end{pmatrix} \tag{6}$$