Indian Institute of Technology, Guwahati
Guwahati, INDIA 781 039

Department of Chemistry — Date: 27 November 2017; 2:00-5.00 p.m.

CH-101 — **End-Semester Exam** — **Maximum Marks = 60**

Name: Division: Signature of Invigilator:

Roll No.: Signature of Student

Answer only in this sheet. Only fully correct answers will be accepted. All questions are compulsory. Rough work is mandatory

1. Given the Planck's radiation law $\rho(\upsilon) = \frac{8\pi h\upsilon^3}{c^3}\frac{1}{\frac{h\upsilon}{e^{kT}}-1}$ and $\frac{N_2}{N_1} = e^{-\Delta E/kT} = e^{-h\upsilon/kT}$, the relationship between Einstein A and B coefficients i.e., A/B would be: **2.0 Marks**

~~(Z)~~	(Y) $\frac{8\pi h}{\lambda^3}$	~~(X)~~	~~(W)~~

2. The angle between the two hybridized orbitals $\Psi_1 = 0.45\,\Psi_{2s} + 0.71\,\Psi_{2p_y} + 0.55\,\Psi_{2p_z}$ and $\Psi_1 = 0.45\,\Psi_{2s} - 0.71\,\Psi_{2p_y} + 0.55\,\Psi_{2p_z}$ is, **2.0 Marks**

~~(H) 180.0°~~	~~(G) 120.0°~~	~~(E) 109.0°~~	(F) 104.5°

3. The C-H bond (harmonic oscillator) vibrational frequency is 9.0 x 10^{13} Hz. The force required to stretch the C-H bond (harmonic oscillator) by 0.2 Å is 250 pN. The vibrational frequency of the C-H bond in Hz is: **2.0 Marks**

(C) 9.0 x 10^{13}	~~(B) 9.0 x 10^{12}~~	~~(A) 4.5 x 10^{12}~~	~~(D) 4.5 x 10^{13}~~

4. A proton (1.67×10^{-27} kg) is confined in an infinite one-dimensional square well of width 10 fm (1 fm = 10^{-15} m). h = 6.62 × 10^{-34} Js; c = 3.0 × 10^8 ms^{-1}. The approximate wavelength of the photon (in fm) emitted when the proton undergoes a transition from the second excited state (n = 3) to the first excited state (n = 2) is: **2.0 Marks**

~~(K) 242~~	~~(I) 303~~	(L) 121	~~(J) 202~~

5. Butadiene molecule is a conjugated molecule and can be considered (for particle-in-a-box model) to be linear with length of 578 pm. With the mass of electron, 9.109 x 10^{-31} kg and Planck's constant being 6.626 x 10^{-34} Js, the absorbance band due to energy difference of 9.02 x 10^{-19} J would be due to transitions between quantum states, **2.0 Marks**

~~(O) 1 and 2~~	(M) 2 and 3	~~(P) 3 and 4~~	~~(N) 4 and 5~~

6. For a two-electron system when the spatial part of the wavefunction is $\Psi_+ = \left[\frac{1}{\sqrt{2}}\{\Psi_a(r_1)\Psi_b(r_2) + \Psi_b(r_1)\Psi_a(r_2)\}\right]$, the spin-part of the wavefunction can then be written as **2.0 Marks**

(Q) $\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$	~~(R) $\frac{1}{\sqrt{2}}\alpha(1)\beta(2)$~~	~~(S) $\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$~~	~~(T) $\frac{1}{\sqrt{2}}\beta(1)\alpha(2)$~~

7. For a solution of 10% transmission at 600 nm, the absorbance (A) is **2.0 Marks**

~~(U) 0.1~~	(A) 1.0	~~(V) 10.0~~	~~(B) 100.0~~

8. If the wave function for an electron circulating on a ring could be written as $\Psi(\varphi) = Ae^{im\varphi}$, then the value of A would be,

~~(Y) $\sqrt{2\pi}$~~	~~(B) $1/\sqrt{\pi}$~~	(A) $1/\sqrt{2\pi}$	~~(Z) $\sqrt{2/\pi}$~~	**2.0 Marks**

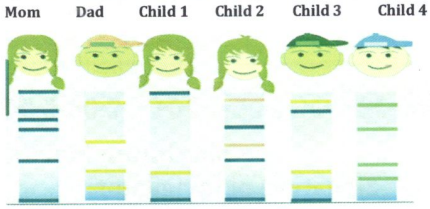
9. Given the Planck's radiation law expressed in wavelength, $\rho(\lambda)d(\lambda) = \frac{8\pi hc}{\lambda^5}\frac{1}{\frac{hc}{e\lambda kT}-1}\,d(\lambda)$ and considering $\lambda \ll \frac{hc}{kT}$, the wavelength at which the radiation would be maximum (λ_{max}) is, **2.0 Marks**

~~(C) $\frac{8hc}{5kT}$~~	~~(D) $\frac{hc}{kT}$~~	(V) $\frac{hc}{5kT}$	~~(X) $\frac{5hc}{kT}$~~

10. For nitrogen molecule at room temperature (T = 300 K), the typical rotational transition frequency is 30 GHz and $\delta\nu/\nu = 2.3\times10^{-6}$; where $\delta\nu = \frac{2\nu}{c}\left(\frac{2kTln2}{m}\right)^{1/2}$. The linewidth would be about **2.0 Marks**

~~(U) 70 GHz~~	~~(E) 70 Hz~~	~~(F) 70 MHz~~	(T) 70 kHz

11. Look at the DNA profiling of Mom and Dad and compare it with the children (1-4) and tell which of the statements are true (T) and which are false (F). **2.0 Marks**



	(T)/(F)
(H) Child 2 is child of Mom but not Dad	(T)
(S) Child 1 and Child 4 are brother and sister	(F)
(R) Child 1 and Child 3 are children of both Mom and Dad	(T)
(G) Child 4 is not the child of Mom and Dad	(T)

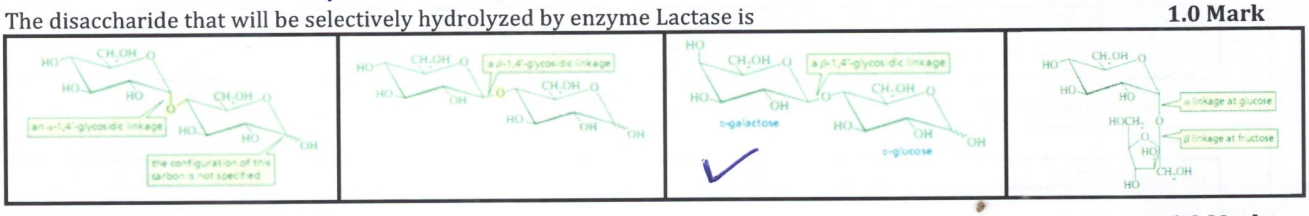
12. The world-famous scientist Stephen Hawking is suffering from **1.0 Mark**

(Q)	Parkinson disease	(I) ✓	Huntington's disease	(J)	Down's syndrome	(P)	Tay-Sachs

13. Which of the DNA sequence is NOT palindromeic? **1.0 Mark**

(K)	5'-GAATTC-3' 3'-CTTAAG-5'	(L) ✓	5'-GAAUUC-3' 3'-CTTAAG-5'	(N)	5'-CTTAAG-3' 3'-GAATTC-5'	(M)	5'-ACCGGT-3' 3'-TGGCCA-5'

14. The disaccharide that will be selectively hydrolyzed by enzyme Lactase is **1.0 Mark**



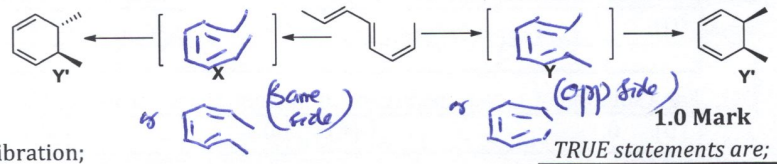
15. Among the following statements, **1.0 Mark**
    (i) Aspartame is a disaccharide;
    (ii) Sucralose is a disaccharide;
    (iii) Inverted sugar is sweeter than normal sugar;
    (iv) Gentamicin is a carbohydrate based antibiotic;
    (v) Plaque substance dextran has β-1,3′ and β-1,3′ glycosidase linkage

FALSE statements are;	
(H)	(i), (iii) and (v)
(G)	(ii), (iv) and (v)
(F)	(i), (iii) and (iv)
(E) ✓	(i) and (v) only

16. Among the following statements, **1.0 Mark**
    (i) A thermal reaction takes place without the absorption of light;
    (ii) A molecular orbital is antibonding, if the number of bonding interaction is same as the number of nodes;
    (iii) For 1,3,5,7-octatriene system it has same number of π-bonding & π-antibonding MO;
    (iv) In pericyclic reactions, reactants are in excited state for both thermal & photochemical reactions;
    (v) A conjugated triene when undergo electrocyclic reactions will have lower λmax.

TRUE statements are;							
(H) ✓	(i), (iii) & (v)	(G)	(ii), (iv) & (v)	(F)	(i), (iii) & (iv)	(E)	(i) & (v) only

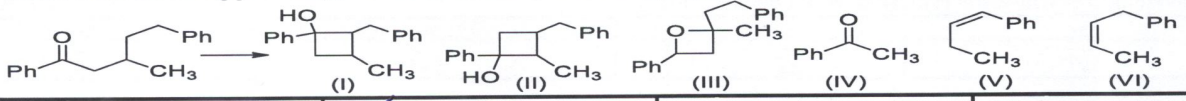
17. Draw the configuration of photoisomerized triene (*X*) & (*Y*) that would lead to products (*X′*) & (*Y′*) under thermal condition. **1.0 Mark**



18. Among the following statements, **1.0 Mark**
    (i) Photoexcitation is slower than molecular vibration;
    (ii) A triplet sensitizer excites another molecule to its triplet state only;
    (iii) A sensitizer absorb light of same wavelength to that of the molecule it will excite subsequently;
    (iv) During photoreduction of benzophenone to benzopinacol isoproponal is converted to acetone;
    (v) Chemical yield is measure of number of molecules undergoing particular process

TRUE statements are;	
(H)	(i), (iii) and (v)
(G) ✓	(ii), (iv) and (v)
(F)	(i), (iii) and (iv)
(E)	(i) and (v) only

19. Which of the following product(s) will be obtained by Norrish type II path; **1.0 Mark**

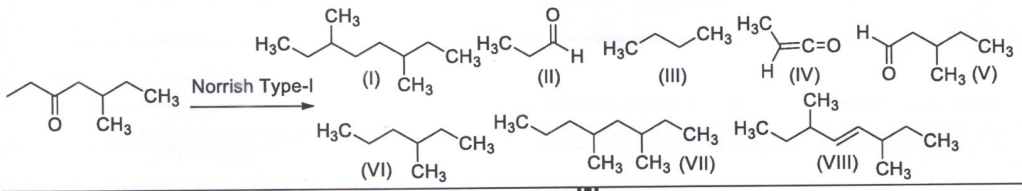


(Q)	(ii), (iv) and (vi)	(I) ✓	(i), (iv) and (vi)	(J)	(ii), (iv) and (v)	(P)	(iii), (iv) and (vi)

20. Name the following photochemical process **1.0 Mark**

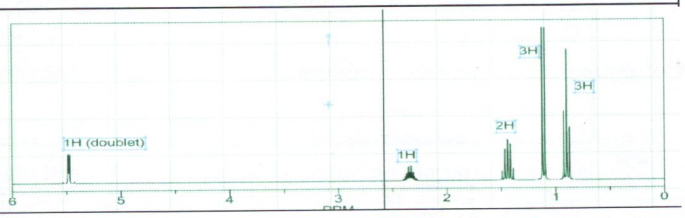
(i)	$S_1 \rightarrow S_o$	FLUORESCENCE	(ii)	$S_n^* \rightarrow S_n$	VIBRATIONAL RELAXATION
(iii)	$S_1^* \rightarrow T_1$	INTER SYSTEM CROSSING	(iv)	$T_1 \rightarrow S_o$	PHOSPHORESCENCE

21. **1+1 Marks**

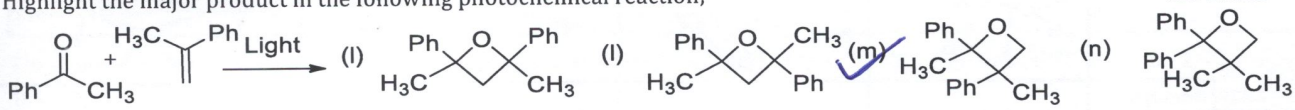


Which of the products will be obtained by Norrish type I path (both primary and secondary process?	
(M)	(ii), (iii), (iv), (v) and (vii) only
(N)	(i), (ii), (iii), (vi) and (vii) only
(O) ✓	(i), (ii), (iii), (iv), (v) and (vi) only
(P)	(i), iii), (iii), (v) and (viii) only

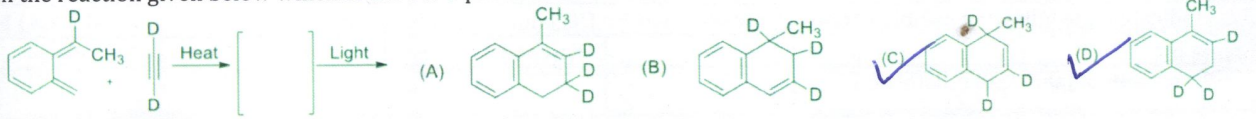
Which of the above compounds (I-VIII) shall have the following ^1H NMR spectra. Answer: (VIII)



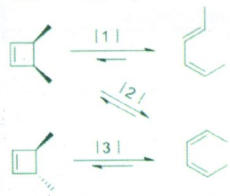
22. Highlight the major product in the following photochemical reaction; **1.0 Mark**



23. In the reaction given below which of the TWO products will NOT be obtained. **1.0 Mark**

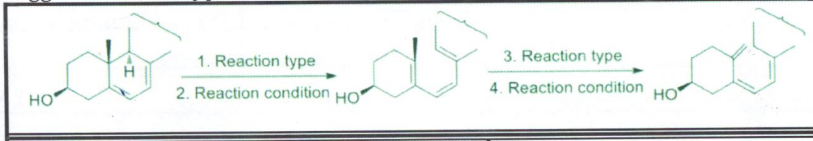


24. Suggest appropriate reaction conditions (thermal or photochemical) for the following interconversions. **1.0 Mark**

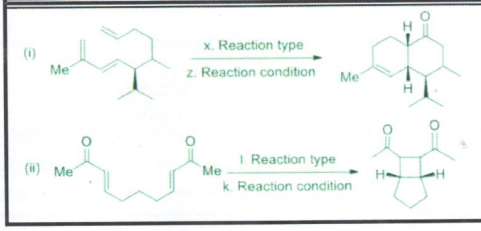


|1|	THERMAL
|2|	PHOTOCHEMICAL
|3|	THERMAL

25. Suggest the exact types of reaction (including numbering) / conditions for the following **1.0 + 1.0 Marks**

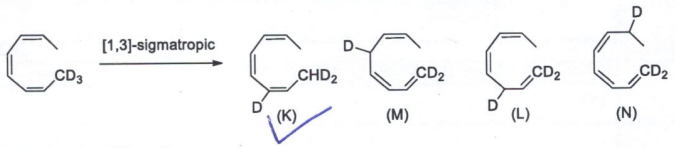


1.	Electrocyclic
2.	Photochemical
3.	[1,7] Sigmatropic
4.	Thermal

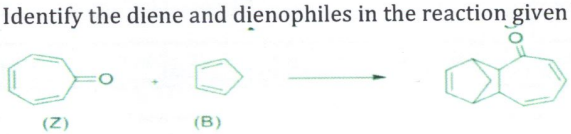


X.	[4+2] cycloaddition
Z.	Thermal.
I.	[2+2] cycloaddition
K.	Photochemical

26. Which one of the following product will NOT be obtained when the following deuterared substrate undergo 1,3-sigmatropic rearrangement(s). **1.0 Mark**



27. Identify the diene and dienophiles in the reaction given below **1.0 Mark**



(Z) DIENOPHILE

(B) DIENE

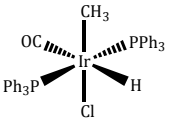
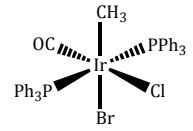
28. Generate 18 electron homoleptic complexes of Mn, Ti, Cr and V with CO as ligand and arrange them in the increasing order of their carbonyl stretching frequency ν_{CO} **2 Marks**

$[Ti(CO)_6]^{2-} < [V(CO)_6]^{-} < [Cr(CO)_6] < [Mn(CO)_6]^{+}$

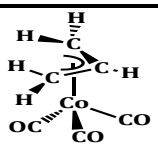
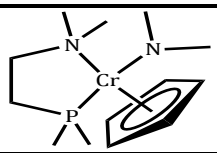
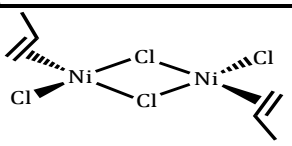
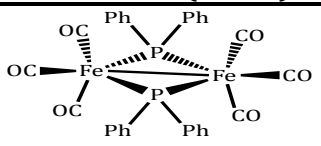
29. Arrange the complexes $Mo(CO)_3(PR_3)$ with R = OMe, Cl, F and Ph in the increasing order of their M-C bond strength **1 Mark**

$Mo(CO)_3(PF_3) < Mo(CO)_3(PCl_3) < Mo(CO)_3(P(OMe)_3) < Mo(CO)_3(PPh_3)$

30. Draw the product obtained when Vaska's complex $[IrCl(CO)(PPh_3)_2]$ is reacted with (i) CH_4 and (i) CH_3Br **1 + 1 Marks**

(i) 	(ii) 

31. Indicate the number of valence electron on each metal complex. **(0.5 X 4) Marks**

				
Electron Count	18	17	16	18

32. Indicate if the following exhibit Strong (S), Weak (W) or No (N) Jahn-Teller distortion **(0.5 X 4) Marks**

	$[Fe(ox)_3]^{3-}$	$[Fe(en)_3]^{3+}$	$[Ti(H_2O)_6]^{3+}$	$[Cr(H_2O)_6]^{2+}$
Strength of Jahn-Teller distortion	N	W	W	S

33. In the MO approach, the frontier orbitals for an O_h complex with σ-donor ligands are t_{2g}(non-bonding) and $e_g(\sigma^*)$ respectively. Indicate the corresponding frontier orbitals in the case of π-donating and π-accepting ligands **2 Marks**

π-donating Ligands $t_{2g}(\pi^*)$ and $e_g(\sigma^*)$	π-accepting Ligands $t_{2g}(\pi)$ and $e_g(\sigma^*)$

34. Assign the transitions for the following bands observed in the electronic absorption spectrum of $[CrF_6]^{3-}$ **2 Marks**

670 nm Transition: $^4A_{2g} \rightarrow {}^4T_{2g}$	440 nm Transition: $^4A_{2g} \rightarrow {}^4T_{1g}$ *(F)*	290 nm Transition: $^4A_{2g} \rightarrow {}^4T_{1g}$ *(P)*

35. The respective ground state term for $[CuCl_4]^{2-}$ and $[Cu(H_2O)_6]^{2+}$ are **2 Marks**

~~(U) ^2E and $^2T_{2g}$~~	~~(V) ^2E_g and $^5T_2$~~	(X) $^2T_2$ and ^2E_g	~~(Y) $^5T_2$ and ^5E_g~~

36. Using Slater's rules, calculate the effective nuclear charge for a *3d* and a *4s* electron in vanadium **1 Mark**

3d electron 4.30	*4s* electron 3.30

37. The magnitude of the difference in the CFSE (ignoring pairing energy), of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ is **1 Mark**

(U) 2.0 Δ_O	~~(V) 1.0 Δ_O~~	~~(X) 0.0 Δ_O~~	~~(Y) 3.3 Δ_O~~

38. Arrange the complex ions, ($[Cr(NH_3)_6]^{3+}$, $[CrCl_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, $[Cr(CN)_6]^{3-}$) in the decreasing order of their wavelength of absorption **1 Mark**

$[CrCl_6]^{3-} > Cr(H_2O)_6]^{3+} > [Cr(NH_3)_6]^{3+} > [Cr(CN)_6]^{3-}$

39. Draw and name the molecular geometry of $[XeOF_5]^-$. **1 Mark**

(i) 	(ii) pentagonal pyramidal or pentagonal monopyramidal

40. Arrange the elements (B, F, Li, C, N, O and Be) in the increasing order of their first ionization potential. **1 Mark**

Li < B < Be < C < O < N < F