# 210

#### CHEMISTRY-CY

### Q.1 - Q.25: Carry ONE mark each.

- 1. For an enzyme catalyzed reaction, the plot of inverse of initial rate against inverse of initial substrate concentration is linear with slope 0.16 s and intercept  $2.12 \text{ mol}^{-1}\text{L}$  s. The estimated value of Michaelis constant (in mol L<sup>-1</sup>, rounded off to two decimal places) is \_\_\_\_\_\_
- 2. When three moles of helium is mixed with one mole of neon at constant temperature and pressure (25°C, 1 atm), the entropy of mixing (in JK<sup>-1</sup>, rounded off to two decimal places) is \_\_\_\_\_
- 3. Fluorescence quantum yield and fluorescence lifetime of a molecule are 0.4 and  $5\times10^{-9}$  s, respectively. If the fluorescence decay rate constant is  $Y\times10^7$  s<sup>-1</sup>, the vlaue of Y (rounded off to nearest ineger) is
- 4. In oxyhemocyanin, the coordination number, mode of oxygen binding, color and the net magnetic behaviour of copper ions, respectively are [Given: atomic number of Cu is 29)
  - (a) Five,  $\mu \eta^2 O_2^-$ , colorless and paramagnetic
  - (b) Five,  $\mu \eta^2 \eta^2 O_2^{2-}$ , blue and diamagnetic
  - (c) Four,  $\mu \eta^1 \eta^1 O_2^-$ , colorless and paramagnetic
  - (d) Four,  $\mu \eta^1 \eta^1 O_2^{2-}$ , blue and diamagnetic.
- 5. The maximum number of microstates for d<sup>2</sup> electronic configuration is \_\_\_\_\_
- 6. At 25°C, the emf (in volts, rounded off to three decimal places) of the cell,  $Ag \mid AgBr(s) \mid Br^{-}(a=0.20)$ ,  $Cu^{2+}(a=0.48)$ ,  $Cu^{+}(a=0.24) \mid Pt$  is \_\_\_\_\_\_
- (Given: The standard emf of the cell is 0.082 V;  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $F = 96500 \text{ C mol}^{-1}$ )
- 7. The correct statement regarding the substitution of coordinated ligands in Ni(CO)<sub>4</sub> and Co(NO)(CO)<sub>3</sub> is (Given: Co–N–O bond is nearly linear; atomic numbers of Co and Ni are 27 and 28, respectively)
  - (a) Both Ni(CO)<sub>4</sub> and Co(NO)(CO)<sub>3</sub> follow associative pathway.
  - (b) Ni(CO)<sub>4</sub> and Co(NO)(CO)<sub>3</sub> follow dissocitive and associative pathways, respectively
  - (c) Ni(CO)<sub>4</sub> and Co(NO)(CO)<sub>3</sub> follow associative and dissociative pathways, respectively
  - (d) Both Ni(CO)<sub>4</sub> and Co(NO)(CO)<sub>3</sub> follow dissociative pathway.
- 8. The activity of 'm' molal CuSO<sub>4</sub> solution can be expressed in terms of its mean activity coefficient  $(\gamma_{\pm})$  as
  - (a)  $16 \, m^4 \gamma_{\pm}^4$
- (b)  $4 m^3 \gamma_{\pm}^3$
- (c)  $m^2 \gamma_{\pm}^2$
- (d)  $108 \, m^5 \gamma_+^5$

9. Major product formed in the given reaction is

$$\alpha$$
-D-glucose  $\frac{\text{acetone(excess)}}{\text{H}^+}$ 



- 10. For a cubic crystal system, the powder X-ray diffraction pattern recorded using Cu  $K_{\alpha}$  source  $(\lambda = 1.54 \text{ Å})$  shows a peak at 33.60°  $(2\theta)$  for (111) plane. The lattice parameter 'a' (in Å, rounded off to two decimal places) is \_\_\_\_\_\_
- 11. The character table for a pyramidal  $AB_3$  molecule of  $C_{3v}$  point group is given below:

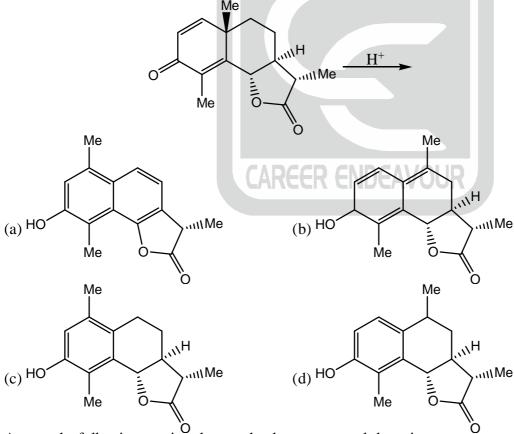
$C_{3v}$	E	$2C_{3}$	$3\sigma_v$		
$\overline{A_1}$	1	1	1	z.	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	-
E	2	-1	0	$(x,y)(R_x,R_y)$	$\frac{x^2 + y^2, z^2}{\left(x^2 - y^2, xy\right)(xz, yz)}$

The reducible representation of pyramidal AB<sub>3</sub> is

$$\begin{array}{c|cccc} C_{3\nu} & E & 2C_3 & 3\sigma_{\gamma} \\ \hline \Gamma & 12 & 0 & 2 \end{array}$$

The correct option representing all the normal Raman active modes of pyramidal AB<sub>3</sub> is (a)  $2A_1 + 2E$  (b) 3E (c)  $3A_1 + A_2 + E$  (d)  $A_1 + A_2 + 2E$ 

12. Major product formed in the following reaction is



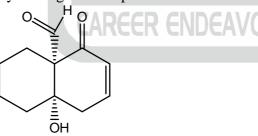
Among the following species, the one that has pentagonal shape is [Given: atomic number of O, F, S, I and Xe are 8, 9, 16, 53 and 54, respectively]

- (a)  $\left[ XeF_{5} \right]^{-}$
- (b) XeOF<sub>4</sub>
- (c) IF<sub>5</sub>
- (d)  $\left[ SF_{5} \right]^{-}$



14. In the following reaction sequence,

15.



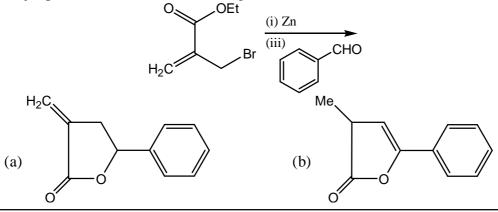
(a) 4aS, 8aR

(b) 4aR, 8aS

(c) 4aR, 8aR

(d) 4aS, 8aS

Major product formed in the following transformation is 16.





$$(c) \qquad (d) \qquad (d)$$

17. In an NMR spectrometer operating at a magnetic field strength of 16.45 T, the resonance frequency (in MHz, rounded off to one decimal place) of <sup>19</sup>F nucleus is \_\_\_\_\_\_

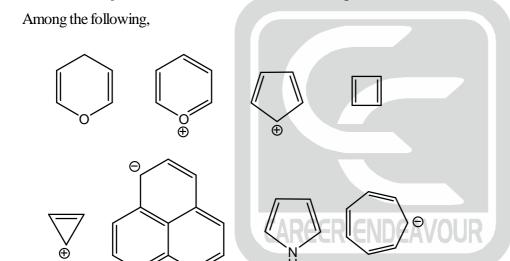
[Given: g factor of  $^{19}$ F = 5.255;  $\beta_N = 5.05 \times 10^{-27} \ J \ T^{-1}$ ;  $h = 6.626 \times 10^{-34} \ Js$ ]

18. Among the following, the suitable reagents for the given transformation is:

- (a) NaBH<sub>4</sub>/CeCl<sub>3</sub>.7H<sub>2</sub>O
- (c) Li/Liq. NH<sub>3</sub>

19.

- (b)  $H_2N-NH_2/KOH$ ,  $\Delta$
- $(d) H_2$ , Pd/C



The total number of aromatic species is \_\_\_\_\_

- 20. In a uranium recovery process, an aqueous solution of uranyl ion is evaporated, dried in air at 400°C and subsequently reduced with hydrogen at 700°C to obtain a uranium compound (X). The oxidation state of uranium in X is \_\_\_\_\_\_ [Given: atomic number of U is 92]
- 21. Major product formed in the following reaction sequence is



$$(b) \begin{picture}(b){0.5\textwidth} \hline (b){0.5\textwidth} \hline (b){0.5\textwidth} \hline (c){0.5\textwidth} \hline (c$$

- 22. A solution containing a metal complex absorbs at 480 nm with molar extinction coefficient of 15,  $000 \text{ L mol}^{-1}\text{cm}^{-1}$ . If the path length of the cell is 1.0 cm and transmittance is 20.5 %, the concentration (in mol L<sup>-1</sup>) of the metal complex is
  - (a)  $1.37 \times 10^{-5}$
- (b)  $4.59 \times 10^{-5}$
- (c)  $8.75 \times 10^{-5}$
- (d)  $2.29 \times 10^{-5}$
- 23. Among the following linear combination of atomic orbitals, the **CORRECT** representation of the lowest unoccupied  $\pi$ -molecular orbital of butadiene is

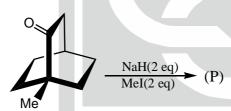
(a) 
$$\psi = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$

(b) 
$$\psi = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$

(c) 
$$\psi = -0.372\phi_1 + 0.602\phi_2 - 0.602\phi_3 + 0.372\phi_4$$

(d) 
$$\psi = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$

24. In the following reaction,



the number of peaks exhibited by the major product (P) in its broadband proton decoupled  $^{13}C$  NMR spectrum is

- 25. The CORRECT statement about hexagonal boron nitride is
  - (a) It is reactive towards fluorine
  - (b) It has same layer stacking as that of graphite
  - (c) It is a good electrical conductor
  - (d) It has lower thermal stability in air compared to that of graphite.

## Q.26 - Q.55: Carry TWO marks each.

26. The rate of solvolysis of the given compounds is in the order:









(S)





$$X = \begin{cases} 0 \\ X = \\ -\xi = 0 \end{cases}$$
  $NO_2$ 

(a) R > T > Q > S > P

(b) Q > T > R > P > S

(c) T > Q > R > P > S

- (d) T > R > Q > S > P
- 27. Assuming no interaction between vibrational and rotational energy levels in HF, the frequency (in cm<sup>-1</sup>, rounded off to the nearest integer) of the R branch line originating from J = 4 in its IR spectrum is

[Given: Rotational constant for HF = 19.35 cm<sup>-1</sup>;  $\overline{v}_0 = 4138.52 \text{ cm}^{-1}$ ]

- 28. The total number of g|| lines expected in the EPR spectrum of a solution of bis (salicylaldimine) coppper (II) having pure <sup>63</sup>Cu and <sup>14</sup>N at 77K is \_\_\_\_\_\_ [Given: I values of <sup>63</sup>Cu, <sup>14</sup>N and <sup>1</sup>H are 3/2, 1 and 1/2, respectively]
- 29. Major product formed in the following synthetic sequence is

30. Major products (P) and (Q), formed in the reactions given below are

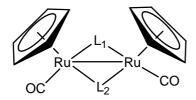
Me 
$$Ag_2O$$
  $P$ 

Me  $Ag_2O$   $P$ 

Me  $Ag_2O$   $Q$ 



The **CORRECT** combination of L1 and L2 among H<sup>-</sup>, NO<sup>-</sup>, MeCH<sup>2-</sup> and CO, that will satisfy the 18 31. electron rule for both metal centers in the following neutral molecule is



(Given: atomic number of Ru is 44)

- (a) MeCH<sup>2-</sup>, CO
- (b) H-, NO
- (c) MeCH<sup>2-</sup>, NO<sup>-</sup>
- (d) H<sup>-</sup>, CO

In the electronic absorption spectrum of an aqueous solution of  $\left[ \text{Ni} \left( \text{NH}_3 \right)_6 \right]^{2+}$ , a very weak band is 32. observed between the bands due to the transitions  ${}^3A_{2g} \longrightarrow {}^3T_{2g}$  and  ${}^3A_{2g} \longrightarrow {}^3T_{lg}(F)$ . The transition responsible for the very weak band is [Given: atomic number of Ni is 28)

(a) 
$${}^{3}A_{2g} \longrightarrow {}^{1}E_{g}$$

$$(b) {}^{3}A_{2g} \longrightarrow {}^{1}T_{2}$$

$$(c) {}^{3}A_{2g} \longrightarrow {}^{1}T_{1}$$

CAREER ENDEAVOUR

(a) 
$${}^{3}A_{2g} \longrightarrow {}^{1}E_{g}$$
 (b)  ${}^{3}A_{2g} \longrightarrow {}^{1}T_{2g}$  (c)  ${}^{3}A_{2g} \longrightarrow {}^{1}T_{1g}$  (d)  ${}^{3}A_{2g} \longrightarrow {}^{1}A_{2g}$ 

The van der Waals constants a and b for gaseous CO are given as 1.49  $L_2$  atm mol<sup>-2</sup> and 0.0399 L 33. mol<sup>-1</sup>, respectively. The fugacity (in atm, rounded off to two decimal places) of CO at 35°C and 95 atm is [Given:  $R = 0.082 L atm K^{-1} mol^{-1}$ ).

Among the following. 34.

$$\left[B_{12}H_{12}\right]^{2^{-}}, \left[Ni_{5}\left(CO\right)_{12}\right]^{2^{-}}, \left[C_{2}B_{9}H_{11}\right]^{2^{-}}, Rb_{6}\left(CO\right)_{16}, Os_{6}\left(CO\right)_{20}, B_{5}H_{11}, B_{6}H_{10}$$
 the total number of species having nido structure is \_\_\_\_\_\_   
 [Given: atomic numbers of H, B, C, O, Ni, Rh and Os are 1, 5, 6, 8, 28, 45 and 76, respectively]

35. The following table lists the reaction/conversion catalyzed by metalloenzymes.

#### Reaction/conversion

(P) 
$$R - H + O_2 + 2H^- + 2e^- \rightarrow R - OH + H_2O$$

- (Q)  $O_2 + 4e^- + 8H^+ \rightarrow 2H_2O + 4H^+$
- $(R) 2H_2O_2 \rightarrow 2H_2O + O_2$
- (S)  $NH_2 CH_2 CO_2H \rightarrow NH_2 CH(CH_2OH) CO_2H$

- Metalloenzyme
- (I) Co-enzyme B<sub>12</sub>
- (II) Cytochrome P-450
- (III) Cytochrome c oxidase
- (IV) Catalase

The **CORRECT** combination is

(a) P-IV, Q-III, R-II, S-I

(b) P-II, Q-III, R-IV, S-I

(c) P-I, Q-IV, R-III, S-II

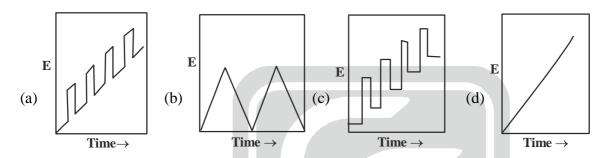
(d) P-II, Q-I, R-III, S-IV



36. Among the following,

the total number of compounds showing characteristics carbonyl stretching frequency less than  $1700\,\mathrm{cm^{-1}}$  in their IR spectra is \_\_\_\_\_

37. The **CORRECT** 'voltage (E) versus time' excitation signal used in cyclic voltammetry is



- 38.  $\Delta G_f^0$  and  $\Delta H_f^0$  for Fe(g) are 370.7 kJ mol<sup>-1</sup> and 416.3 kJ mol<sup>-1</sup> at 298 K, respectively. Assuming  $\Delta H_f^0$  is constant in the interval 250 K to 375 K,  $\Delta G_f^0$  (rounded off to the nearest integer) for Fe(g) at 375 K is (a) 325 kJ mol<sup>-1</sup> (b) 338 kJ mol<sup>-1</sup> (c) 310 kJ mol<sup>-1</sup> (d) 359 kJ mol<sup>-1</sup>
- The frequency (in cm<sup>-1</sup>, rounded off to two decimal places) for pure rotational in the spectrum of NO molecule due to change in the quantum number from J=1 to J=2 is [Given: Moment of inertia of NO =  $1.6427 \times 10^{-16}$  kg m<sup>2</sup>;  $h=6.626\times 10^{-34}$  J s;  $c=3\times 10^8$  m/s]
- 40. For the ring opening reaction of cyclopropane to propene at 25°C, the pre-exponential factor is  $4.3\times10^{15}$  s<sup>-1</sup>. The entropy of activation (in JK<sup>-1</sup> mol<sup>-1</sup>, rounded off to two decimal places) is \_\_\_\_\_ [Given:  $h = 6.626\times10^{-34}$  Js;  $k_B = 1.38\times10^{-23}$  JK<sup>-1</sup>; R = 8.314 JK<sup>-1</sup>mol<sup>-1</sup>]
- 41. In the following reaction sequence, the major product (A) and (R) are

$$\mathsf{Me} \xrightarrow{\mathsf{SiMe}_3} (\mathsf{Q})$$

$$\mathsf{Me} \xrightarrow{\mathsf{(i)} \ (\mathsf{Ph}_3\mathsf{P})_2\mathsf{PdCl}_2, \ \mathsf{CuI}, \ \mathsf{Et}_3\mathsf{N}, \ \Delta}} (\mathsf{P})$$

$$\mathsf{Major \ product}$$

$$\mathsf{(iii)} \ \mathsf{O}_{\mathsf{BH}}$$

$$\mathsf{Major \ product}$$

$$\mathsf{(iii)} \ \mathsf{NaOMe} (\mathsf{R})$$



(a) Me 
$$\longrightarrow$$
 and Me  $\longrightarrow$  (R)

(c) Me 
$$\longrightarrow$$
 and Me  $\longrightarrow$  (R)

- 42. The experimental magnetic moment (3.4 BM) of a hydrated salt of Eu<sup>3+</sup> at 27°C is significantly different from the calculated value. The difference is due to [Given: atomic number of Eu is 63)
  - (a) Population of electrons at higher J level(s) via thermal excitation
  - (b) Pairing of electrons in f-orbitals
  - (c) strong ligand field splitting of f-orbitals
  - (d) strong spin-orbit coupling
- 43. Adsorption of N<sub>2</sub> on TiO<sub>2</sub> was carried out at 75 K. A plot of  $\frac{z}{(1-z)V}$  versus  $z(z=p/p^0)$  gives a straight line with an intercept,  $4.0 \times 10^{-6}$  mm<sup>-3</sup> and slope,  $1.0 \times 10^{-3}$  mm<sup>-3</sup>. The volume (rounded off to the nearest integer) corresponding to the monolayer coverage is

  (a) 555 mm<sup>3</sup> (b) 690 mm<sup>3</sup> (c) 996 mm<sup>3</sup> (d) 785 mm<sup>3</sup>
- 44. The CORRECT statement with respect to the stereochemistry of α-hydroxy acids P and Q formed in the following reaction is

$$(P) \xrightarrow{OH} Me \xrightarrow{Br} CO_2H \xrightarrow{Ag_2O} (Q)$$

$$H_2O, OH$$

- (a) P is formed with inversion of configuration and Q with retention of configuration
- (b) P is formed with retention of configuration and Q with inversion of configuration
- (c) Both P and Q are formed with retention of configuration
- (d) Both P and Q are formed with inversion of configuration



45. Major product formed in the following reaction sequence is

46. A compound with molecular formula  $C_{10}H_{12}O_2$  showed a strong IR band at -1720 cm<sup>-1</sup>, a peak at m/z 122 in the mass spectrum and the following <sup>1</sup>H NMR signals :  $\delta$  8.1–8.0 (2H, m), 7.6–7.5 (1H, m), 7.5–7.3 (2H, m), 4.3 (2H, t), 1.8 (2H, sextet) and 1.0 (3H, t). The structure of the compound is

- 47. At 30°C, the vapor pressure and density of a 1.0 M aqueous solution of sucrose are 31.207 mm Hg and 1.1256 g/mL, respectively. If the vapor pressure of pure water at 30°C is 31.824 mm Hg, the activity coefficient (rounded off to three decimal places) of water in the given solution is \_\_\_\_\_ [Given: The molar mass of sucrose = 342.3 g mol<sup>-1</sup>)
- 48. Among the following sets,



Ph.....Ph Ph Ph.....Ph and 
$$\frac{1}{\underline{\underline{\underline{H}}}}$$
  $\frac{\underline{\underline{\underline{H}}}}{\underline{\underline{\underline{H}}}}$  Me Me Me Me

the total number of set(s) of diaster eomeric pair(s) is

The % error (rounded off to two decimal places) in the ground state energy of a particle in a one dimensional 49. box of length 'a' described by a trial variation function  $\varphi = x(a-x)$ , where  $0 \le x \le a$ , is \_\_\_\_

[Given: The true ground state energy of the above system is  $h^2/8 ma^2$ ;  $\int \varphi^* \varphi d\tau = a^5/30$ )

Major products (P) and (Q), in the given reaction sequence, are 50.

$$CO_2Et \xrightarrow{(i) 9-BBN (1 \text{ eq.})} (P) \xrightarrow{(i) MsCl/Et_3N} (Q)$$

$$(ii) NaOH$$

$$(iii) NaOH$$

$$(iii) H_2, (Ph_3P)_3RhCl$$

(a) 
$$CO_2Et$$
 and  $CO_2Et$  and  $CO_2Et$   $CO_2ET$ 

(c) 
$$(P)$$
  $(Q)$   $(Q)$ 

The fission reaction of  ${}^{235}_{92}U$  with thermal neutron is represented below. 51.

 $^{99}_{41}\,\mathrm{Nb}\,$  and  $^{133}_{51}\,\mathrm{Sb}\,$  are the primary fission fragment pair, which undergo series of radioactive decay to form stable nuclei  $\boldsymbol{X}_{\!\scriptscriptstyle 3}$  and  $\boldsymbol{Y}_{\!\scriptscriptstyle 4}$  (chain enders). The  $\boldsymbol{X}_{\!\scriptscriptstyle 3}$  and  $\boldsymbol{X}_{\!\scriptscriptstyle 4}$ , respectively are

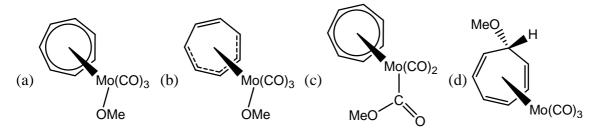
- (a)  $^{87}_{35}$ Br and  $^{124}_{43}$ Tc (b)  $^{99}_{44}$ Ru and  $^{133}_{55}$ Cs (c)  $^{93}_{38}$ Sr and  $^{127}_{35}$ Ag (d)  $^{96}_{41}$ Nb and  $^{130}_{51}$ Sb



- 52. Consider that A gX crystallizes in rock salt structure. The density of AgX is 6477 kg/m³ and unit cell length is 577.5 pm. Atomic weight of Ag is 107.87 g mol<sup>-1</sup>. The atomic weight of X (in g mol<sup>-1</sup>, rounded off to two decimal places) is \_\_\_\_\_
- 53. In the following reaction sequence,

$$\frac{\text{NaOMe}}{\text{Mo(CO)}_3} \xrightarrow{\text{NaOMe}} (A) \xrightarrow{50^{\circ}\text{C}} (B)$$

The structure of B is (Given: atomic number of Mo is 42)



54. The hydrogen-like radial wave function of the 3s orbital is given as

$$R_{3.0} = \frac{1}{9\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - 2\rho + \frac{\rho^2}{9}\right) e^{-\rho/6}$$

where,  $\rho = \frac{2Zr}{a_0}$ ; Z = atomic number; r = distance from the nucleus and  $a_0 =$  Bohr radius

Positions of the radial nodes (in units of  $a_0$ ) of the 3s orbital are at

(a) 
$$\frac{3+\sqrt{3}}{2Z}$$
,  $\frac{3-\sqrt{3}}{2Z}$  (b)  $\frac{6+3\sqrt{3}}{2Z}$ ,  $\frac{6-3\sqrt{3}}{2Z}$  (c)  $\frac{3+3\sqrt{3}}{2Z}$ ,  $\frac{3-3\sqrt{3}}{2Z}$  (d)  $\frac{9+3\sqrt{3}}{2Z}$ ,  $\frac{9-3\sqrt{3}}{2Z}$ 

In a reaction, reactant X is converted to products Y and Z consecutively with rate constants  $6.0 \times 10^{-2}$  min<sup>-1</sup> and  $9.0 \times 10^{-3}$  min<sup>-1</sup>, respectively. If the initial amount of X is 12.5 moles, the number of moles (rounded off to one decimal place) of Y formed after 10 minutes is \_\_\_\_\_\_

\*\*\*\*\* END OF THE QUESTION PAPER \*\*\*\*\*

