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**TARGET : JEE (ADVANCED) 2015**

Course : VIJETA & VIJAY (ADP & ADR)

Date : 28-04-2015

**PHYSICAL CHEMISTRY**

**DPP**

DAILY PRACTICE PROBLEMS

**NO. 07**

**TEST INFORMATION**

DATE : 29.04.2015

PART TEST (PT) - 3

**Syllabus : Inorganic :** s & p-Block Element, Metallurgy **Organic :** Aromatic compound, Carbonyl Compounds, Carboxylic acids & their derivatives, Grignard Reagent.

**DPP No. # 07 (JEE-ADVANCED)**

Total Marks : 169

Max. Time : 137 min.

|  |                   |           |
|--|-------------------|-----------|
| Single choice Objective (–1 negative marking) Q.1 to Q.15            | (3 marks 2½ min.) | [45, 37½] |
| Multiple choice objective (–1 negative marking) Q.16 to Q.20         | (4 marks, 3 min.) | [20, 15]  |
| Assertion and Reason (‘–1’ negative marking) Q.21 to Q.23            | (3 marks 2½ min.) | [09, 7½]  |
| Comprehension (–1 negative marking) Q.24 to Q.32                     | (3 marks 2½ min.) | [27, 22½] |
| Match Listing (–1 negative marking) Q.33                             | (8 marks, 3 min.) | [08, 08]  |
| Single Digit Subjective Questions (no negative marking) Q.34 to Q.38 | (4 marks 2½ min.) | [20, 12½] |
| Double Digits Subjective Questions (no negative marking) Q.39 to 42  | (4 marks 2½ min.) | [16, 10]  |
| Match the column (4 vs 4) (no negative marking) Q.43 to Q.45         | (8 marks, 8 min.) | [24, 24]  |

- The time of decay for thermonuclear reaction is given by  $t = 5 \times t_{1/2}$ . The relation between mean life T and time of decay t is given by :  
(A)  $2T \ln 2$  (B)  $5T \ln 2$  (C)  $2T \ln 2$  (D)  $1/2 \ln 2$
- Two first order reaction have half-lives in the ratio 8:1. Calculate the ratio of time intervals  $t_1 : t_2$ . The time  $t_1$  and  $t_2$  are the time period for  $\left(\frac{1}{4}\right)^{\text{th}}$  completion of 1<sup>st</sup> reaction and  $\left(\frac{3}{4}\right)^{\text{th}}$  completion of 2<sup>nd</sup> reaction respectively.  
(A) 1 : 0.301 (B) 0.125 : 0.602 (C) 1 : 0.62 (D) none of these
- The reaction  $A(g) + 2B(g) \rightarrow C(g)$  is an elementary reaction. In an experiment involving this reaction, the initial partial pressures of A and B are  $P_A = 0.40$  atm and  $P_B = 1.0$  atm respectively. When pressure of C becomes  $(P_C) = 0.3$  atm in the reaction the rate of the reaction relative to the initial rate is :  
(A)  $\frac{1}{12}$  (B)  $\frac{1}{50}$  (C)  $\frac{1}{25}$  (D) none of these
- Initial concentration of reaction for nth order reaction is 'a'. Which of the following relations is correct about  $t_{1/2}$  of the reaction ?  
(A)  $\ln t_{1/2} = \ln (\text{constant}) - (n - 1) \log_e a$  (B)  $\ln t_{1/2} = \ln (\text{constant}) - \ln a$   
(C)  $t_{1/2} \ln n = \ln (\text{constant}) + \ln a_0$  (D)  $\ln t_{1/2} = n \ln a_0$



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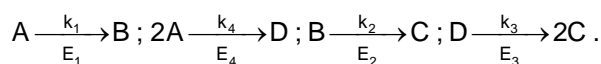
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PAGE NO.-1

5. Heptene decomposes according to following reaction
- $$\text{C}_7\text{H}_{14} \xrightarrow{\Delta} 2\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$$
- Rate constant was found to be  $1 \times 10^{-4} \text{ sec}^{-1}$ . In what time (approximately) molar ratio of heptene to ethene in the reaction mixture will attain the value 1?  
 $[\log 2 = 0.3010, \log 3 = 0.4771]$   
 (A) 68 min (B) 4055 min (C) 1736 min (D) 228 min
6. When the concentration of A is doubled, the rate for the reaction :  $2\text{A} + \text{B} \rightarrow 2\text{C}$  quadruples. When the concentration of B is doubled the rate remains the same. Which mechanism below is consistent with the experimental observations ?  
 (A) Step I :  $2\text{A} \rightleftharpoons \text{D}$  (fast equilibrium)  
 Step II :  $\text{B} + \text{D} \rightarrow \text{E}$  (slow)  
 Step III :  $\text{E} \rightarrow 2\text{C}$  (fast)  
 (B) Step I :  $\text{A} + \text{B} \rightleftharpoons \text{D}$  (fast equilibrium)  
 Step II :  $\text{A} + \text{D} \rightarrow 2\text{C}$  (slow)  
 (C) Step I :  $\text{A} + \text{B} \rightarrow \text{D}$  (slow)  
 Step II :  $\text{A} + \text{D} \rightleftharpoons 2\text{C}$  (fast equilibrium)  
 (D) Step I :  $2\text{A} \rightarrow \text{D}$  (slow)  
 Step II :  $\text{B} + \text{D} \rightarrow \text{E}$  (fast)  
 Step III :  $\text{E} \rightarrow 2\text{C}$  (fast)
7. The reaction  $\text{A} \xrightarrow{k} \text{Product}$ , is zero order reaction while the reaction  $\text{B} \xrightarrow{k} \text{Product}$ , is first order reaction. For what initial concentration of A are the half lives of the two reactions equal ?  
 (A)  $(\log_e 4) \text{ M}$  (B)  $2\text{M}$  (C)  $\log 2\text{M}$  (D)  $\ln 2 \text{ M}$
8. Which of the following statements are correct :  
 (1) Order of a reaction can be known from experimental results and not from the stoichiometry of reaction.  
 (2) Molecularity a reaction refers to (i) each of the elementary steps in (an overall mechanism of) a complex reaction or (ii) a single step reaction.  
 (3) Overall order of a reaction  $m\text{A} + n\text{B} \rightarrow \text{AB}_x$  is  $m + n$ .  
 Select the correct answer using the following codes.  
 (A) 2 and 3 (B) 1, 2 and 3 (C) 1, 3 (D) 1, 2
9. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize sodium atom . Then ionisation energy of sodium atom :  
 (A) 494.73 kJ/mol (B) 494.73 kJ/atom  
 (C) 637.2 kJ/mol (D) 637.2 kJ/atom
10. The Schrodinger wave equation for an orbital in hydrogen atom is given as
- $$\psi(\text{radial}) = \frac{1}{16\sqrt{4}} \left( \frac{Z}{\alpha_0} \right)^{3/2} [(\sigma - 1)(\sigma^2 - 8\sigma + 12)] e^{-\sigma/2}$$
- Where  $\alpha_0$  and Z are the constant in which answer can be expressed and  $\sigma = \frac{2Zr}{\alpha_0}$ , then nearest and farthest position of radial nodes from nucleus are ..... respectively.
- (A)  $\frac{\alpha_0}{Z}, \frac{3\alpha_0}{Z}$  (B)  $\frac{\alpha_0}{2Z}, \frac{\alpha_0}{Z}$  (C)  $\frac{\alpha_0}{2Z}, \frac{3\alpha_0}{Z}$  (D)  $\frac{\alpha_0}{2Z}, \frac{4\alpha_0}{Z}$

11. Consider the 1<sup>st</sup> order reactions :



$E_1, E_2, E_3$  and  $E_4$  are respective activation energies and  $k_1, k_2, k_3$  and  $k_4$  are respective rate constants. Which of the following is not correct ?

(A)  $\frac{d[B]}{dt} = k_1[A] - k_2[B]$  (B)  $\frac{d[C]}{dt} = k_2[B] + 2k_3[D]$

(C) Average activation energy of  $A = \frac{k_1E_1 + k_4E_4}{k_1 + k_4}$  (D) None of these

12. Difference between  $n^{\text{th}}$  and  $(n + 1)^{\text{th}}$  Bohr's radius of H-atom is equal to its  $(n - 1)^{\text{th}}$  Bohr's radius. The value of  $n$  is :

- (A) 1 (B) 2 (C) 3 (D) 4

13. The half-life of  $^{99}\text{Tc}$  is 6.0 h. The total residual activity in a patient after receiving an injection containing  $^{99}\text{Tc}$  must not be more than 0.01  $\mu\text{Ci}$ , after 36.0 hours. What is the maximum activity (in  $\mu\text{Ci}$ ) that the sample injected can have ?

- (A) 0.06 (B) 0.16 (C) 0.32 (D) 0.64

14. The angular momentum of an electron in a Bohr's orbit of H-atom is  $4.2178 \times 10^{-34} \text{ kgm}^2/\text{sec}$ . Calculate the wavelength of the spectral line emitted when electrons falls from this level to next lower level.

- (A)  $1.8 \times 10^{-5} \text{ cm}$  (B)  $1.8 \times 10^{-4} \text{ cm}$  (C)  $1.8 \times 10^{-4}$  (D)  $1.8 \times 10^{-5} \text{ m}$

15. The uncertainty in speed of a moving atom of mass 200 amu is 100 m/s. What is the minimum uncertainty in the measurement of its position ? (1 amu =  $1.6 \times 10^{-24} \text{ g}$  ;  $h = 6.4 \times 10^{-34} \text{ J sec}$ )

- (A)  $1.1 \times 10^{-10} \text{ m}$  (B)  $1.59 \times 10^{-12} \text{ m}$  (C)  $1.01 \times 10^{-8} \text{ m}$  (D)  $1.53 \times 10^{-6} \text{ m}$

16. For a certain reaction  $A \longrightarrow \text{products}$ , the  $t_{1/2}$  as a function of  $[A]_0$  is given as below :

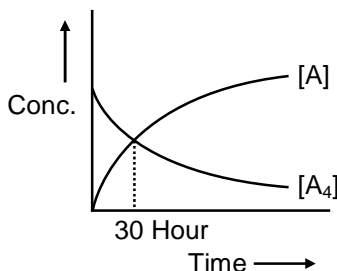
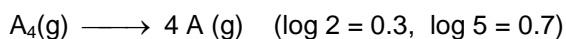
$[A]_0 \text{ (M)} :$  0.1 0.025

$t_{1/2} \text{ (min.)} :$  100 50

Which of the following is/are true ?

- (A) The order is  $\frac{1}{2}$  (B)  $t_{1/2}$  would be  $100\sqrt{10} \text{ min}$  for  $[A]_0 = 1 \text{ M}$   
(C) The order is 1 (D)  $t_{1/2}$  would be 100 min for  $[A]_0 = 1 \text{ M}$

17. Consider the following first order decomposition and the accompanying concentration – time plot :



Which of the following statements regarding the decomposition reaction is/are true ?

- (A) At 30 hrs , only 20 % reaction is complete.  
(B) Half –life of the reaction is 90 hrs (approximately).  
(C) Rate of decomposition decreases linearly with time.  
(D) Changing initial concentration will change the time at which the two curves are intersecting.

18. Element 'A' has principal quantum number 2 for last electron and it has 3 electron in valence shell and element 'B' has principal quantum number 3 for last electron and it has seven electrons in the valence shell. The atomic number of an element X is equal to sum of atomic numbers of A and B. Which of the following statement is/are correct for X ?  
 (A) M shell contain 10 electrons  
 (B) Total number of electrons with  $l=1$  are 12  
 (C) Total number of electrons with  $m=0$  may be 14  
 (D) It can show back bonding in which d orbitals are involved.
19. Which of the following do not represent ground state configuration of given element ?  
 (A) Sc- [Ar]  $3d^3 4s^0$  (Z=21) (B) Si- [Ne]  $3s^2 3p^2$  (Z=14)  
 (C) Cu- [Ar]  $3d^9 4s^2$  (Z=29) (D) La- [Xe]  $6s^2 4f^1$  (Z=57)
20. The magnetic moment of  $X^{n+}$  is  $\sqrt{24}$  BM. Hence, the species can be  
 (A)  $Fe^{2+}$  (B)  $Cr^{2+}$  (C)  $Mn^{2+}$  (D)  $Co^{3+}$
21. **Statement-1** : For zero order reaction ( $A \rightarrow B$ ), successive half life of reaction decreases with the progress of reaction.  
**Statement-2** : Rate of zero order reaction remains unchanged with the progress of reaction.  
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True
22. **Statement-1**: The maximum degeneracy of an electron for which azimuthal quantum number is  $l$  is  $(2l + 1)$ .  
**Statement-2** : For a given value of  $l$ , the magnetic quantum number ( $m$ ) can have any integral value in the range of  $-l$  to  $+l$ .  
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True
23. **Statement-1** : The shortest wavelength of transition of Lyman series is observed when electron jumps from orbit no.  $n = \infty$  to  $n = 1$ .  
**Statement-2**: The wavelength of transition is given by  $\lambda = \frac{hc}{\Delta E}$   
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True

### Comprehension # 1

#### DEFINITION VALID FOR SINGLE ELECTRON SYSTEM :

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV / atom} \quad (\text{Energy of electron in } n^{\text{th}} \text{ orbit of hydrogen like species having atomic number } Z)$$

#### (i) Ground state :

Lowest energy state of any atom or ion is called ground state of the atom It is  $n = 1$ .

**(ii) Excited State :**

States of atom other than the ground state are called excited states :

|             |                               |
|-------------|-------------------------------|
| $n = 2$     | first excited state           |
| $n = 3$     | second excited state          |
| $n = 4$     | third excited state           |
| $n = n + 1$ | $n^{\text{th}}$ excited state |

**(iii) Ionisation energy (IE) :**

Minimum energy required to move an electron from ground state to

$n = \infty$  is called ionisation energy of the atom or ion.

**(iv) Excitation Energy :**

Energy required to move an electron from ground state of the atom to any other state of the atom is called

excitation energy of that state.

Excitation energy of 2<sup>nd</sup> state = excitation energy of 1<sup>st</sup> excited state = 1<sup>st</sup> excitation energy =  $E_2 - E_1$

**(v) Binding Energy 'or' Separation Energy :**

Energy required to move an electron from any state to  $n = \infty$  is called binding energy of that state.

Binding energy of ground state = I.E. of atom or Ion.

The third excitation energy of a hydrogen like species is 204 eV.

24. Identify the hydrogen like species.

- (A)  $\text{He}^+$  (B)  $\text{Li}^{2+}$  (C)  $\text{Be}^{3+}$  (D)  $\text{B}^{4+}$

25. What is the binding energy of  $e^-$  from second state in the given species ?

- (A) 13.6 eV (B) 54.4 eV (C) 122.2 eV (D) 17 eV

26. If ionisation energy is 'a' eV then ionisation potential is 'a' V. Using this information, find the ionisation potential of given species.

- (A) 54.4 V (B) 217.6 V (C) 122.4 V (D) 13.6 V

**Comprehension # 2**

For a particular reaction at constant temperature,  $\text{A(g)} + 2\text{B(g)} \longrightarrow \text{products}$

Following rate information were recorded :

| Exp No. | Initial [A] | Initial [B] | Initial rate [ $\text{M min}^{-1}$ ] |
|---------|-------------|-------------|--------------------------------------|
| 1.      | 1.00        | 1.00        | 1.00                                 |
| 2.      | 2.00        | 4.00        | 8.00                                 |
| 3.      | 3.00        | 9.00        | 27.00                                |
| 4.      | 4.00        | 2.00        | ?                                    |

On the basis of following observation give the answer of the following questions

27. Which of the following is the correct rate law for the given reaction ?

- (A)  $R = k[\text{A}][\text{B}]^2$  (B)  $R = k[\text{A}]^2[\text{B}]$  (C)  $R = k[\text{A}]^2[\text{B}]^{1/2}$  (D)  $R = k[\text{A}]^{1/2}[\text{B}]^2$

28. What is the rate of reaction in the 4<sup>th</sup> experiment ?

- (A)  $15.3 \text{ M min}^{-1}$  (B)  $22.4 \text{ M min}^{-1}$  (C)  $29.4 \text{ M min}^{-1}$  (D)  $36 \text{ M min}^{-1}$

**Comprehension # 3**

A definite volume of  $\text{H}_2\text{O}_2$  undergoing decomposition required 22.8 mL of standard  $\text{KMnO}_4$  solution for titration. After 10 and 20 min, the volumes of permanganate required were 13.8 and 8.25 mL, respectively.

Given  $\ln \frac{228}{138} = 0.05$  and  $\ln \frac{2280}{825} = 1.01$

29. Find order of reaction.  
 (A) 1 (B) 2 (C) 3 (D) 3/2
30. Calculate the time (in. min) required for the decomposition to be half completed.  
 (A) 1.8 (B) 7.6 (C) 13.7 (D) 20.4

#### Comprehension # 4

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve

electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidized metal surface thickness  $(1-f)$  relative to the maximum thickness  $(T)$  of oxidized surface, when metal surface is exposed to air for a considerable period of time.

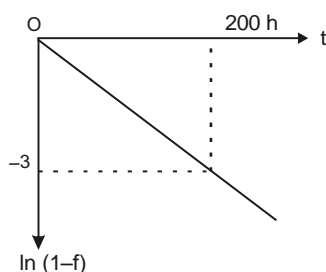
Rate law :  $\frac{df}{dt} = k(1-f)$ ,

where  $f = x/T$ ,

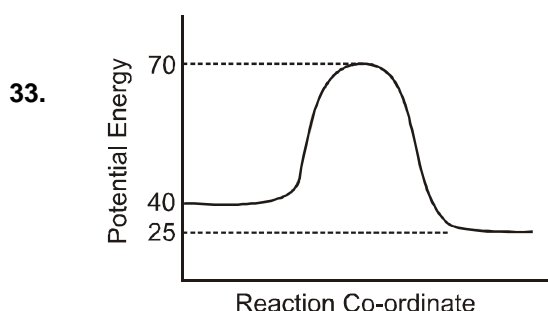
$x$  = thickness of the oxide film at time 't'

and  $T$  = thickness of the oxide film at  $t = \infty$

For the oxidation of a particular metal, a graph is shown in the figure.



31. The time taken for thickness to grow 50% of  $T$  is  
 (A) 23.1 h (B) 46.2 h (C) 100 h (D) 92.4 h
32. The exponential variation of  $f$  with  $t$  (h) is  
 (A)  $f = (1 - e^{-3t/200})$  (B)  $f = (1 - e^{-3t/200} - 1)$  (C)  $f = e^{-3t/200}$  (D)  $f = e^{3t/200}$



Match the following column :

Column-I

- (P) Activation energy of forward reaction  
 (Q) Threshold energy  
 (R) Activation energy for backward reaction  
 (S) Enthalpy change of the reaction

Column-II

- (1) 70 kJ mol<sup>-1</sup>  
 (2) 30 kJ mol<sup>-1</sup>  
 (3) 15 kJ mol<sup>-1</sup>  
 (4) 45 kJ mol<sup>-1</sup>

|     | P | Q | R | S |
|-----|---|---|---|---|
| (A) | 1 | 4 | 3 | 2 |
| (C) | 1 | 2 | 3 | 4 |

|     | P | Q | R | S |
|-----|---|---|---|---|
| (B) | 2 | 1 | 4 | 3 |
| (D) | 2 | 1 | 3 | 4 |



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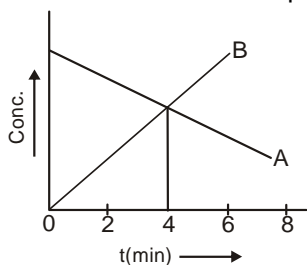
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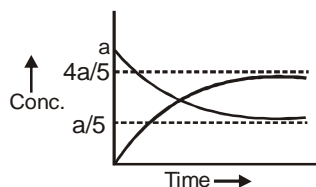
PAGE NO.-6

34. For zero order reaction  $A \rightarrow 3B$  plot of concentration vs time is as follows.



Find half life period in minutes if the initial concentration of A be 1 M.

35. Find the total number of alpha particles and neutrons emitted when  $^{12}\text{C}$  is bombarded on  $^{139}_{57}\text{La}$  to produce  $^{147}_{63}\text{Eu}$ . (Assume no other particles are produced)
36. Calculate the maximum total number of electrons in Gallium, with spin  $+\frac{1}{2}$  and which occupy orbitals having minimum one radial node.
37.  $^{238}_{92}\text{U}$  is bombarded with  $^b_a\text{X}$  particle to produce  $^{238}_{93}\text{Np}$  and two neutrons. The Np thus formed is unstable and decays to produce  $^{238}_{94}\text{Pu}$  along with a particle  $^d_c\text{Y}$ . Find  $a + b + c + d$
38. A reversible reaction which is 1<sup>st</sup> order in both direction  $A \xrightleftharpoons[K_2]{K_1} B$ . For which value of  $\frac{K_1}{K_2}$  following graph will be correct (where a is initial amount of reactant A)



39. Consider the first order parallel reactions, starting with 1 M of A.
- $$A \xrightarrow{3k} B \quad ; \quad A \xrightarrow{2k} 2C \quad ; \quad A \xrightarrow{k} 3D$$
- If  $[C]_{\infty}$  is x M, find 100 x.
40.  $^{24}_{11}\text{Na}$  (half-life = 15 hrs) is known to contain some radioactive impurity (half-life = 3 hrs) in a sample. This sample has an initial activity of 1000 counts per minute, and after 30 hrs it shows an activity of 200 counts per minute. What percent of the initial activity was due to the impurity
41.  $^{58}\text{Zn}$  decays by two paths. By path (I), it produce daughter nuclide 'X' along with a positron and proton. By path(II) it produce daughter nuclide 'Y' along with a positron. Find the sum of neutrons in X and Y.
42. The hydration of ethylene oxide ( $\text{C}_2\text{H}_4\text{O}$ ) in aqueous solution proceeds with first order kinetics such that ethylene glycol is formed. The kinetics of the equation is determined by measuring the change in volume of the liquid system. The change in volume is noted by measurement of height at various instants in a thin capillary tube. From the data, calculate the rate of disappearance of ethylene dioxide at an initial concentration of 22 g/L. Express answer in terms of M/day.

|             |    |                    |          |
|-------------|----|--------------------|----------|
| Time        | 0  | 3600               | $\infty$ |
| Height (mm) | 11 | $1 + \frac{10}{e}$ | 1        |



43. Match the following :
- $E_n$  = total energy
- $\ell_n$  = angular momentum in  $n^{\text{th}}$  orbit
- $K_n = \text{K.E.}$  ,  $V_n = \text{P.E.}$
- $T_n$  = time period,  $r_n$  = radius of  $n^{\text{th}}$  orbit

**Column (I)**

- (a)  $E_n^{-y} \propto r_n$  then y, for a fixed Z, is
- (b)  $\ell_n \propto n^x$  then x is
- (c)  $\frac{E_n}{V_n}$  is
- (d)  $T_n \propto \frac{Z^t}{n^m}$ , t and m respectively are

**Column (II)**

- (p)  $\frac{1}{2}$
- (q)  $-2$
- (r)  $-3$
- (s) 1

44. Match entries in column-I with those in column-II for a radioactive sample :

**Column-I**

- (A) Activity of sample
- (B) Half life of sample
- (C) Number of radioactive nuclei
- (D) Decay constant

**Column-II**

- (p) varies with time
- (q) varies with temperature.
- (r) is a constant for a given species at any time and temperature
- (s) its log vs time graph is a straight line

45. Match the following :

|     | Column-I  |     | Column- II  |
|-----|---|-----|---|
| (a) | $t_{1/2} \propto a^{-1}$ (a = initial concentration of reactants) | (p) | $E_f < E_b$ ( $E_f$ and $E_b$ are activation energies of forward and backward reaction)   |
| (b) | Rate constant (k) has unit = $\text{L mol}^{-1} \text{s}^{-1}$    | (q) | Order of reaction is 0.   |
| (c) | Equilibrium constant (K) has infinitely large value.              | (r) | Order of reaction is 2.   |
| (d) | $t_{1/2}$ decreases linearly with time                            | (s) | $[A] = \frac{[A]_0}{1 + kt[A]_0}$<br>$[A]_0$ = initial concentration ,<br>$[A]$ = instantaneous concentration ,<br>k = rate constant. |



## CHEMISTRY

- $t = 5 \times t_{1/2} = 5 \times \frac{\ln 2}{\lambda} = 5 T \ln 2$   
 Hence, (B) is the correct answer.
- $t_1 = \frac{(t_{1/2})_1}{0.693} \ln \left( \frac{1}{1 - (1/4)} \right)$  ;  $t_2 = \frac{(t_{1/2})_2}{0.693} \ln \left( \frac{1}{1 - 3/4} \right)$  ;  $\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\ln(4/3)}{\ln(4)} = 1 : 0.62$
- $$\begin{array}{ccccccc} \text{A(g)} & + & 2\text{B(g)} & \rightarrow & \text{C(g)} & & \\ t = 0 & & 0.4 \text{ atm} & & 1 \text{ atm} & & 0 \text{ atm} \\ t = t & & (0.4 - 0.3) \text{ atm} & & (1 - 0.6) \text{ atm} & & 0.3 \text{ atm} \end{array}$$
 Since reaction is elementary.  
 So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient  
 $\text{Rate} = K [\text{A}] [\text{B}]^2$  ;  $\text{Rate}_{(\text{Initial})} = K [0.4] [1]^2$  ;  $\text{Rate}_{(\text{after } t = t)} = K [0.1] [0.4]^2$   
 $\frac{R_{(t=t)}}{R_{(t=0)}} = \frac{K[0.1][0.4]^2}{K[0.4][1]^2} = \frac{1}{25}$
- $t_{1/2} \propto \frac{1}{a^{n-1}}$  ;  $t_{1/2} = k \frac{1}{a^{n-1}}$  ;  $\ln t_{1/2} = \ln k - (n - 1) \log_e a$ .  
 Hence, (A) is the correct answer.
- $$\begin{array}{ccc} \text{C}_7\text{H}_{14} & \rightarrow & 2\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 \\ a & & 0 \quad 0 \\ a - x & & 2x \quad x \end{array}$$
 $\frac{a-x}{2x} = 1, x = \frac{a}{3}$  ;  $1 \times 10^{-4} = \frac{2.303}{t} \log \frac{a}{2a/3}$  ;  $t = 67.59 \text{ min.}$
- The information suggest that rate =  $k[\text{A}]^2$   
 This is satisfied by (D),  
 In (A) and (C) B is involved in slow step, ; In (B), if we solve, B will appears in rate law.
- For zero order reaction,  $x = kt$  ;  $\therefore \frac{a}{2} \times k \times t_{1/2}$  i.e.  $t_{1/2} = \frac{a}{2k}$  ....(i)  
 For first order reaction,  $t_{1/2} = \frac{\log_e 2}{k}$  ....(ii)  
 From (i) and (ii),  $\frac{a}{2k} = \frac{\log_e 2}{k}$  ;  $a = \log_e 4 \text{ M}$  ; Hence, (A) is the correct answer.
- Fact based
- $\text{I.E.} = \frac{n h c}{\lambda} = \frac{(6.022 \times 10^{23}) \times (6.62 \times 10^{-34})}{242 \times 10^{-9}} \times 3 \times 10^8 = 494.730 \text{ kJ/mol}$
- At nodes,  $\psi = 0$   
 $\Rightarrow (\sigma - 1)(\sigma^2 - 8\sigma + 12) = 12$   $\Rightarrow \sigma = 1 \text{ and } (\sigma - 6)(\sigma - 2) = 0$   
 $\Rightarrow \sigma = 6 \quad \sigma = 2$  ; Nearest radial node  $\sigma = 1$   $\Rightarrow \frac{2Zr}{\alpha_0} = 1$   
 $\Rightarrow r = \frac{\alpha_0}{2Z}$  Farthest radial node  $\sigma = 6$  ;  $\Rightarrow r = \frac{3\alpha_0}{Z}$

11. The listed reactions are first order reactions

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B] + 2k_3[D] \quad ; \quad -\frac{d[A]}{dt} = k_1[A] + 2k_4[A] \quad ; \quad k_{\text{eff}} = k_1 + 2k_4$$

$$\Rightarrow E_{\text{eff}} = \frac{k_1 E_1 + 2k_4 E_4}{k_1 + 2k_4}$$

12.  $r_n \propto n^2$

$$\text{But } r_{n+1} - r_n = r_{n-1} \quad ; \quad (n+1)^2 - n^2 = (n-1)^2 \quad ; \quad n = 4$$

Hence, (D) is the correct answer.

13. Activity after 'n' half lives =  $\frac{A_0}{2^n}$  so,  $0.01 = \frac{A_0}{2^6}$  Hence  $A_0 = 0.64 \mu\text{Ci}$

14.  $mvr = \frac{nh}{2\pi}$

$$\frac{nh}{2\pi} = 4.2178 \times 10^{-34} \quad ; \quad n = \frac{4.1278 \times 10^{-34} \times 2 \times 3.14}{6.625 \times 10^{-34}} = 4 \quad ; \quad \frac{1}{\lambda} = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The wavelength for transition from  $n = 4$  to  $n = 3$

$$\frac{1}{\lambda} = 109678 \left[ \frac{1}{3^2} - \frac{1}{4^2} \right] \quad ; \quad \lambda = 1.8 \times 10^{-4} \text{ cm.}$$

15.  $\Delta p = m\Delta v$   
 $= 200 \times 1.6 \times 10^{-24} \times 10^{-3} \times 100 = 3.2 \times 10^{-23} \text{ kgm/sec}$

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad ; \quad \Rightarrow \quad \Delta x \geq \frac{h}{4\pi\Delta p} \quad \Rightarrow \quad \Delta x \geq \frac{6.4 \times 10^{-34}}{4 \times 3.14 \times 3.2 \times 10^{-23}}$$

$$\Rightarrow \Delta x \geq 1.59 \times 10^{-12} \text{ m}$$

16.  $A \rightarrow \text{Products.}$

$$t_{1/2} = [\text{conc.}]^{1-n} \quad ; \quad n \rightarrow \text{order of reaction.} \quad \frac{100}{50} = \left( \frac{0.1}{0.025} \right)^{1-n} \quad 2 = 2 - 2n \Rightarrow 2n = 1$$

$$\Rightarrow n = \frac{1}{2} \quad \text{order of reaction is } \frac{1}{2} \quad ; \quad \frac{100}{t_{1/2}} = \left( \frac{0.1}{1} \right)^{1/2}$$

$$\Rightarrow t_{1/2} = 100\sqrt{10} \text{ min for } [A_0] = 1\text{M. } (t_{1/2} = 100\sqrt{10} \text{ min } [A_0] = 1\text{M})$$

17.  $A_4 \longrightarrow 4A$

$$\begin{array}{ll} a & 0 \\ a-x & 4x \end{array}$$

$$\text{At 30 hrs,} \quad \begin{array}{l} a - x = 4x \\ a = 5x \end{array}$$

$$x = \frac{a}{5}$$

Hence reaction is 20% complete.

$$k = \frac{1}{30} \ln \frac{a}{4a/5} \quad ; \quad k = \frac{1}{30} \ln \frac{5}{4}$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2 \times 30}{\ln 5 - \ln 4} = \frac{\log 2 \times 30}{\log 5 - \log 4} = \frac{0.3 \times 30}{0.7 - 0.6} = \frac{9}{0.1} = 90 \text{ hrs}$$

$\Rightarrow$  rate follows exponential decay with time.

In first order reaction,  $t_{x\%}$  is independent of initial concentration.



18. Element A =  $1s^2 2s^2 2p^1$

Element B =  $1s^2 2s^2 2p^6 3s^2 3p^5$  ; atomic number of X =  $5 + 17 = 22$

X is Ti

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$  ; M shell contain  $2 + 6 + 2 = 10$  electron

Total number of electron with  $l = 1$

$$= 6 + 6 = 12$$

Total number of electrons with  $m = 0$

$$= 2 + 2 + 2 + 2 + 2 + 2 + 1 = 13$$

As d orbitals contain electrons, so d orbitals can be involved in back bonding.

19. (A)  $[\text{Ar}] 3d^1 4s^2$  (B)  $[\text{Ar}] 3d^{10} 4s^1$  (D)  $[\text{Xe}] 6s^2 5d^1$

20.  $\sqrt{n(n+2)} = \sqrt{24} \Rightarrow n = 4$

Hence, 4 unpaired electron. ;  $\text{Fe}^{2+} \rightarrow 4$  unpaired electron ( $3d^6$ )

$\text{Cr}^{2+} \rightarrow 3d^4$  (4 unpaired electron) ;  $\text{Mn}^{2+} \rightarrow 3d^5$  (5 unpaired electron)

$\text{Co}^{3+} \rightarrow 3d^6$  (4 unpaired electron) ;  $\sqrt{n(n+2)} = \sqrt{24} \Rightarrow n = 4$

26.  $E_4 - E_1 = 204 \text{ eV}$

$$\Rightarrow \frac{-13.6 \times Z^2}{4^2} + 13.6Z^2 = 204 \quad \Rightarrow \quad Z^2 \times 13.6 \times \frac{15}{16} = 204$$

$$\Rightarrow \quad Z^2 = 204 \times \frac{16}{15} \times \frac{1}{13.6} \quad \Rightarrow \quad Z = 4$$

$$\text{B.E. (2nd State)} = 0 - E_2 = 0 - \left( -13.6 \times \frac{4^2}{2^2} \right)$$

$$= 13.6 \times 4 = 54.4 \text{ eV}$$

$$\text{I.E.} = 0 - E_1 = -E_1 = +13.6 \times \frac{4^2}{1^2} = 217.6 \text{ eV} \quad \Rightarrow \quad \text{Ionisation potential} = 217.6 \text{ V}$$

27.  $r = k[A]^x [B]^y$

$$1 = k \quad \dots(1)$$

$$8 = k(2)^x (4)^y \quad \dots(2)$$

$$27 = k(3)^x (9)^y \quad \dots(3)$$



$$\Rightarrow \frac{1}{8} = \frac{1}{2^x \cdot 2^{2y}} \Rightarrow x + 2y = 3 \quad \text{and} \quad \frac{1}{27} = \frac{1}{3^x \cdot 3^{2y}} \Rightarrow x + 2y = 3$$

$x = 1, y = 2$  does not satisfy this relation. ;  $x = 2, y = 1$  does not satisfy this relation.  
 $x = 2, y = 1/2$  satisfy this relation ;  $x = 1/2, y = 2$  does not satisfy this relation.

So, ans is  $r = k[A]^2 [B]^{1/2}$

$$r = k[A]^x [B]^y$$

$$1 = k \quad \dots(1) \quad 8 = k(2)^x (4)^y \quad \dots(2) \quad 27 = k(3)^x (9)^y \quad \dots(3)$$

$$\Rightarrow \frac{1}{8} = \frac{1}{2^x \cdot 2^{2y}} \Rightarrow x + 2y = 3$$

28.  $r = 1 \times [4]^2 [2]^{1/2}$

$$= 16\sqrt{2} = 22.6 \text{ M/min.}$$

29. Let the order be first order. Then

$$K = \frac{1}{10} \ln \frac{0 - 22.8}{0 - 13.8} = \frac{1}{10} \ln \frac{228}{138} = \frac{1}{10} \ln \frac{114}{69}$$

$$= \frac{1}{10} \times 0.50 = 0.05 \quad ; \quad \text{and} \quad k = \frac{1}{20} \ln \frac{22.8}{8.25} = \frac{1}{20} \times 1.01 = 0.05$$

As both K are similar, assumption is correct. It is a first order reaction.

30.  $t_{1/2} = \frac{\ln 2}{K} = \frac{0.693}{0.05} = 13.86 \text{ minutes.}$

32.  $\int \frac{df}{1-f} = \int k dt$



$$t = 0 \quad 1 \quad 0$$

$$t = t \quad 1 - x \quad 3x$$

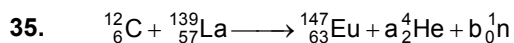
$$\text{at } t = 4, 1 - x = 3x$$

$$x = 1/4$$

for zero order reaction

$$C_t = C_0 - kt \quad ; \quad \frac{3}{4} = 1 - k \times 4 \quad ; \quad 4k = \frac{1}{4} \quad ; \quad k = \frac{1}{16} \quad \text{and} \quad t_{1/2} = \frac{C_0}{2k}$$

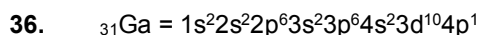
$$t_{1/2} = \frac{1}{2 \times \frac{1}{16}} = 8$$



$$6 + 57 = 63 + 2a$$

$$a=0 \text{ and } 139 + 12 = 147 + b \Rightarrow b = 4$$

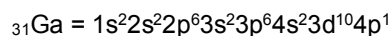
$$\text{Hence } a + b = 4.$$

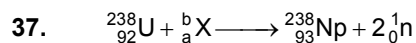


Orbitals having atleast one radial node = 2s, 3s, 3p, 4s, 4p

Hence maximum electrons with spin  $+\frac{1}{2}$

$$= 1+1+3+1+1=7$$





$$b=2, a=1 \quad ; \quad {}_{93}^{238}\text{Np} \longrightarrow {}_{94}^{238}\text{Pu} + {}_c^d\text{Y} \quad ; \quad c=-1, d=0 \quad \Rightarrow \quad a+b+c+d=2$$



$$t = 0 \quad a \quad 0$$

$$t = t \quad a-x \quad x$$

$$t = t_{eq} \quad a - x_{eq} \quad x_{eq}$$

at equilibrium  $\frac{x_{eq}}{a - x_{eq}} = \frac{K_1}{K_2}$  ; From graph  $\frac{K_1}{K_2} = 4$



$$[C]_t = \frac{4k}{3k + 2k + k} [1 - e^{-bkt}] \quad ; \quad [C]_{\infty} = \frac{4k}{6k} [1 - e^{-\infty}] = \frac{2}{3} = 0.67$$

40. Let the activity due to impurity be 'a' cpm.

$\therefore$  due to Na it is  $(1000 - a)$  cpm.

After 30 hrs 'a' would be reduced to  $\left(\frac{1}{2}\right)^{10}$  a cpm

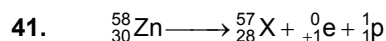
and  $(1000 - a)$  would be reduced to  $\frac{1}{4} (1000 - a)$  cpm

$\therefore$  total activity after 30 hrs would be ;  $\left(\frac{1}{2}\right)^{10} a + \frac{1}{4} (1000 - a) = 200$  (given)

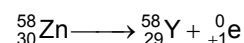
solving we get

$$250 - \frac{1}{4}a \cong 200 \quad \therefore \quad \frac{1}{4}a = 50 \quad \Rightarrow \quad a = 200$$

Hence 20% activity was due to impurity.



$$\text{Neutrons} = 57 - 28 = 29$$



neutrons

=29

$\Rightarrow$  total neutrons in X and Y =  $29 + 29 = 58$

$$42. \quad K = \frac{1}{t} \ln \frac{h_{\infty} - h_0}{h_{\infty} - h_t} = \frac{1}{3600} \ln \frac{1-11}{1-1-\frac{10}{e}}$$

$$= \frac{1}{3600} \ln e = \frac{1}{3600} / \text{sec} = \frac{1}{3600} \times 60 \times 60 \times 24 = 24 / \text{day}$$

$$\Rightarrow \text{rate} = K.[C_2H_4O] = 24 \times \frac{22}{44} = 12 \text{ M/day.}$$

$$-\ln(1-f) = kt + c \quad t = 0, f = 0 \quad -\ln(1-f) = kt$$

From Figure  $k = -\frac{3}{200}$        $f = (1 - e^{-3t/200})$  ;      For 50% grow  $t = \frac{200}{3} \times \ln(0.5) = 46.20\text{h}$

43. (a)  $E_n^{-y} \propto r_n$

$$\left( \frac{Z^2}{n^2} \times 13.6 \text{ eV} \right) \propto \left( \frac{n^2}{Z} \times 0.529 \text{ \AA} \right)$$

$$y = 1$$

(b)  $\ell_n \propto n^x$

$$\frac{nh}{2\pi} \propto n^x$$

$$x = 1$$

(c) Potential energy = 2 total energy

(d)  $T_n \propto \frac{n^3}{Z^2}$        $t = -2$      $m = -3$

44. In radioactive species

(A) Activity =  $\lambda N = \lambda N_0 e^{-\lambda t}$  and  $\lambda$  is independent of temperature and time.

So, Activity varies with time and  $\log(\text{activity}) = \log \lambda N_0 - \frac{\lambda t}{2.303}$

Hence graph is linear.

(B)  $t_{1/2}$  is independent of time and also temperature.

(C)  $N = N_0 e^{-\lambda t}$

Hence, N depends on time and its log vs time graph is straight line.

(D) Explained in (A)

45. (A)  $t_{1/2} \propto \frac{1}{a}$

order is second and  $[A] = \frac{[A_0]}{1 + kt[A_0]}$

(B) Unit of k suggest that order is second and  $[A] = \frac{[A_0]}{1 + kt[A_0]}$

(C)  $K = \frac{k_f}{k_b}$  is infinitely large when  $k_f > k_b$ . This happens when  $E_a$  of forward reaction is less than of backward reaction.

(D) Addition of catalyst increases the rate greatly when the uncatalysed reaction is very slow. i.e. when its activation energy is very large.