# CHEMISTRY

TARGET: JEE Advanced - 2021

# **CAPS - 21**

## **Atomic Structure**

### **Answer Key**

- 1. (C)
- 2.
- (D)
- (A)
- (D)
- 5. (D)

- 6.
- (ACD)
- 7.
  - (ABCD)
- 8. (BCD)
- (ABD)
- **10.** (ABCD)

- 11. (BCD)
- 12.
- (B)
- 13. (B)
- 14. (A)
- **15.**  $(8 \times 10^6)$

- 16. (12)
- 17. (10 amp)
- 18. (300303)
- 19. (1233)
- **20.** (3.00)

- 21. (C)
- 22. (D)

#### Solution

#### SINGLE CHOICE QUESTIONS

For a hypothetical hydrogen like atom, the potential energy of the system is given by  $U(r) = \frac{-Ke^2}{r^3}$ , where r is the distance between the two particles. If Bohr's model of quantization of angular momentum is applicable, then velocity of particle is given by

(A) 
$$v = \frac{n^2 h^3}{K e^2 8 \pi^3 m^2}$$

(B) 
$$v = \frac{n^3 h^3}{8Ke^2 \pi^3 m^2}$$

(C) 
$$v = \frac{n^3 h^3}{24 Ke^2 \pi^3 m^2}$$

(A) 
$$v = \frac{n^2 h^3}{Ke^2 8\pi^3 m^2}$$
 (B)  $v = \frac{n^3 h^3}{8Ke^2 \pi^3 m^2}$  (C)  $v = \frac{n^3 h^3}{24Ke^2 \pi^3 m^2}$  (D)  $v = \frac{n^2 h^3}{24Ke^2 \pi^3 m^2}$ 

Ans.

**Sol.** 
$$\frac{d[U(r)]}{dr} = \frac{3Ke^2}{r^4} \Rightarrow \text{Magnitude of the force}$$

$$\therefore \ \frac{3Ke^2}{r^4} = \frac{mv^2}{r}$$

And we know mvr =  $\frac{\text{nh}}{2\pi}$  or  $r = \frac{\text{nh}}{2\pi \text{m v}}$ 

$$3Ke^2 \times \frac{8\pi^3 m^3 v^3}{n^3 h^3} = mv^2, v = \frac{n^3 h^3}{24Ke^2 \pi^3 m^2}$$

- Calculate the minimum and maximum number of electrons which may have magnetic 2. quantum number, m = +1 and spin quantum number,  $s = -\frac{1}{2}$  in chromium (Cr)
  - (A) 0, 1
- (B) 1, 2
- (C) 4, 6
- (D) 2, 3

Ans. (D)

Sol.



11111

Out of 6 electrons in 2p and 3p must have one electron with m = +1 and s =  $-\frac{1}{2}$  but in 3d subshell an orbital having m = +1 may have spin quantum no.  $-\frac{1}{2}$  or  $+\frac{1}{2}$ 

Therefore, minimum and maximum possible values are 2 and 3 respectively.

- 3. The orbit and orbital angular momentum of an electron are  $\frac{3h}{2\pi}$  and  $\sqrt{\frac{3}{2}} \cdot \frac{h}{\pi}$  respectively. The number of radial and angular nodes for the orbital in which the electron is present are respectively
  - (A) 0, 2
- (B) 2, 0
- (C) 1, 2
- (D) 2, 2

Ans. (A)

**Sol.** Orbit angular momentum  $\frac{nh}{2\pi} = \frac{3h}{2\pi} \Rightarrow n = 3$ 

Orbital angular momentum,  $\sqrt{I(I+1)}\frac{h}{2\pi} = \sqrt{\frac{3}{2}}\frac{h}{\pi} \Rightarrow I = 2$ 

Hence, electron is in 3d-orbital. For 3d-orbital, radial nodes =(n-l-1)=0 Angular nodes =l=2

- **4.** A gaseous mixture contains hydrogen atoms in the 4<sup>th</sup> excited state, He<sup>+</sup> ions in 3<sup>rd</sup> excited state and Li<sup>2+</sup> in 2<sup>nd</sup> excited state. The number of spectral lines obtained in the emission spectrum of this sample when all these atoms/ions return to the ground state is
  - (A) 19
- (B) 20
- (C) 16
- (D) 18

Ans. (D)

**Sol.** No. of spectral lines given by  $H = \frac{5 \times 4}{2} = 10$ 

No. of spectral lines given by  $He^+ = \frac{4 \times 3}{2} = 6$ 

No. of spectral lines given by  $Li^{2+} = \frac{3 \times 2}{2} = 3$ 

However,  $\lambda_{2\rightarrow 1}(H) = \lambda_{4\rightarrow 2}(He^{2+})$ 

Total no. of spectral lines = 10 + 6 + 3 - 1 = 18

#### **MULTIPLE CHOICE QUESTIONS**

- 5. Select incorrect statement(s)
  - (A) Only three quantum numbers n, I and m are needed to define an orbital
  - (B) Four quantum numbers are needed for complete description of an electron
  - (C) Two quantum numbers n and I are needed to identify subshell and shape of orbital
  - (D) Splitting of spectrum lines in presence of electric field is known as Zeeman effect

Ans. (D)

- Sol. Splitting of spectrum lines in presence of electric field is known as Stark effect
- 6. Select the correct statement (s)
  - (A) An electron near the nucleus is attracted by the nucleus and has a low potential energy.
  - (B) According to Bohr's theory an electron continuously radiate energy if it stays in one orbit.
  - (C) Bohr's model could not explain the spectra of multielectron atoms.
  - (D) Bohr's model was first atomic model based on quantization of energy.

Ans. (ACD)

- **Sol.** Bohr gave concept of stationary orbits having fixed energies of electrons.
- **7.** Select the correct statement(s)
  - (A) Lower value of quantum number *l* indicates that there is a higher probability of finding the 3s electron close to the nucleus than those of 3p and 3d electrons
  - (B) Energy of 3s orbital is less than for the 3p and 3d orbitals
  - (C) At the node, the value of the radial function changes from positive to negative
  - (D) The radial function depends upon the quantum numbers n and /

Ans. (ABCD)

**Sol.** Conceptual

- **8.** Select the correct statement (s)
  - (A) Heisenberg's principle is applicable to stationary electron
  - (B) Pauli's exclusion principle is not applicable to photons
  - (C) For an electron the product of velocity and principal quantum number will be independent to principal quantum number
  - (D) Quantum number I and m determine the value of angular wave function

#### Ans. (BCD)

- **Sol.** Heisenberg's principle is applicable for moving electrons.
- 9. Choose the correct statements among the following
  - (A) A node is a point in space where the wave-function  $\Psi$  has zero amplitude
  - (B) The number of maxima (peaks) in radial probability distribution function is (n l)
  - (C) Radial probability density is  $4\pi r^2 R_{nl}^2(r)$
  - (D)  $\Psi^2$  represents probability of finding election

#### Ans. (ABD)

- **Sol.** Radial probability density is  $R_{n_1}^2(r)$
- **10.** Select the correct statement(s) regarding 3py orbital
  - (A) Total number of nodes are 2
  - (B) Number of maxima in the curve  $4\pi r^2 R^2$  vs r are two
  - (C) Quantum number n, I and m for an orbital may be 3, 1, -1 respectively
  - (D) The magnetic quantum number may have a positive value

#### Ans. (ABCD)

**Sol.** Total nodes = (n - 1)

Number of maxima in radial probability distribution function = (n - I)

For given orbital, n = 3, l = 1, m = -1 to +1

- **11.** Select the correct statement (s)
  - (A) Radial function [R (r)] is a part of wave function which depends upon quantum number n only
  - (B) Angular function depends only on the direction, and is independent to the distance from the nucleus
  - (C)  $\Psi^2$  (r,  $\theta$ ,  $\phi$ ) is the probability density of finding the electron at a particular point in space
  - (D) Radial distribution function  $(4\pi r^2 R^2)$  gives the probability of the electron being present at a distance r from the nucleus

#### Ans. (BCD)

Sol. Conceptual.

#### COMPREHENSION # 1 (FOR Q. 12 TO Q.14)

Assume that there were four possible values  $\left(-1, -\frac{1}{2}, +\frac{1}{2}, +1\right)$  for the spin quantum number ms.

Principal quantum number n is defined as usual. However, quantum number I and m, are defined as follows:

I: 1 to (n + 1) in integral steps

ml: - I/2 to +I/2 (including zero, if any) in integral steps

The orbitals corresponding to I = 1, 2, 3, ... designated as A, B, C... respectively.

12. The number of elements that would be present in the second period of the periodic table is (A) 9 (B) 20 (C) 24 (D) 36

Ans. (B)

**Sol.** One orbital can accommodate 4 electrons. Therefore, in second period number of elements 8 + 12 = 20.

13. If Aufbau's principle is not violated i.e. (n + l) rule must be followed, the outermost electronic configuration of an element with atomic number 100 would be

(A) 3B<sup>8</sup>4A<sup>4</sup>

(B) 3C<sup>16</sup>4A<sup>8</sup>

(C) 3C<sup>12</sup>4B<sup>8</sup>

(D) 4B<sup>12</sup>5A<sup>8</sup>

Ans. (B)

Sol.

n value	l values	m values	(n+l)
n = 1	A) <i>l</i> = 1	$-\frac{1}{2}$ , $+\frac{1}{2}$	2
	B) <i>l</i> = 2	-1, 0, +1	3
n = 2	A) <i>l</i> = 1	$-\frac{1}{2}$ , $+\frac{1}{2}$	3
	B) <i>l</i> = 2	-1, 0, +1	4
	C) <i>l</i> = 3	$-\frac{3}{2}$ , $-\frac{1}{2}$ , $+\frac{1}{2}$ , $+\frac{3}{2}$	5
n = 3	A) <i>l</i> = 1	$-\frac{1}{2}$ , $+\frac{1}{2}$	4
	B) <i>l</i> = 2	-1, 0, +1	5
	C) l = 3	$-\frac{3}{2}$ , $-\frac{1}{2}$ , $+\frac{1}{2}$ , $+\frac{3}{2}$	6
	D) <i>l</i> = 4	-2, -1, 0, +1, +2	7
n = 4	A) <i>l</i> = <i>I</i>	$-\frac{1}{2}$ , $+\frac{1}{2}$	5
	B) <i>l</i> = 2	-1,0,+1	6

 $1A^8,1B^{12},2A^8,2B^{12},3A^82C^{16},3B^{12}4A^8,4A^8,3C^{16}$ 

**14.** The number of sub-orbitals and the maximum number of electrons that can be filled in E-orbitals are respectively

(A) 6, 24

(B) 5, 20

(C) 7, 28

(D) cannot be determined

Ans. (A)

**Sol.** For E orbital, number of sub-orbitals = 6

Number of electrons =  $6 \times 4 = 24$ 

#### **NUMERIC ANSWER TYPE**

15. If the average lifetime of an excited state of H atom is of order 10–8 sec, estimate how many orbits an e- makes when it is in the state n = 2 and before it suffers a transition to n = 1 state.

Ans.  $(8 \times 10^6)$ 

**Sol.** The velocity of the electron n in the second state of H atom is  $v = 1.09 \times 10^8$  cm/s

$$Orbital \ frequency \ = \frac{velocity \ of \ e^-}{2\pi r} = \frac{1.09 \times 10^8 \, cm/s}{2 \times 3.14 \times 0.529 \times 10^{-8} \, cm} = 8.2 \times 10^{14} \, s^{-1}$$

The number of orbits made by the electron =  $8.2 \times 10^{14} \text{s}^{-1} \times 10^{-8} \text{ s} = 8.2 \times 10^{6} \approx 8 \times 10^{6}$ 

16. In a sample of hydrogen atom in ground state electrons make transition from ground state to a particular excited state where path length is five times de-broglie wavelength, electrons make back transition to the ground state producing all possible photons. If photon having 2nd highest energy of this sample can be used to excite the electron in a particular excited state of Li<sup>2+</sup> atom, then find the final excited state of Li<sup>2+</sup> atom.

Ans. (12)

Sol. Since electron goes the state where the path length is 5 times de-Broglie wavelength

$$\Rightarrow 2\pi r = 5\lambda$$

Also 
$$\frac{2\pi r}{n} = \lambda \Rightarrow n = 5$$

Hence electron goes to the 5th state

 $2^{nd}$  highest energy line will be  $4 \rightarrow 1$ 

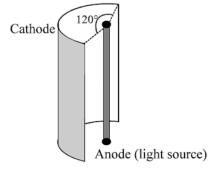
$$13.6\left(1 - \frac{1}{4^2}\right) = 13.6 \times z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$n_1$$
  $n_2$   $3 \rightarrow 12$ 

**17.** A cylindrical source of light which emits radiation radially (from curved surface) only, placed at the center of a hollow cylindrical metallic surface, as shown in diagram.

The power of source is 90 watt and it emits light of wavelength 4000 Å only. The emitted photons strike the cylindrical metallic surface which results in ejection of photoelectrons. All ejected photoelectrons reach to anode (light source). The magnitude of photocurrent is

[Given: 
$$h = 6.4 \times 10^{-34}$$
 J/sec.]



Ans. (10 amp)

**Sol.** Power 90 W = 90 J/s

The energy of one photon =  $\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}} = 4.8 \times 10^{-19}$ 

No. of photons emitted per sec =  $\frac{90}{4.8 \times 10^{-19}} = 1.875 \times 10^{19}$ 

No. of photoelectrons emitted per sec =  $\frac{120}{360} \times 1.875 \times 10^{+19} = 6.25 \times 10^{19}$ 

Current =  $6.25 \times 10^{19} \times 1.62 \times 10^{-19} = 10A$ 

18. Mr. Santa must decode a number "ABCDEF" where each alphabet is represented by a single digit. Suppose an orbital whose radial wave function is represented as  $\Psi_{(r)} = k_1 \cdot e^{-r/k_2} (r^2 - 5k_3r + 6k_3^2)$ 

From the following information given about each alphabet then write down the answers in the form of "ABCDEF", for above orbital.

Info A = Value of n where "n" is principal quantum number

Info B = No. of angular nodes

Info C = Azimuthal quantum number of subshells to orbital belongs

Info D = No. of subshells having energy between (n + 5) s to (n + 5) p where n is principal quantum number

Info E = Orbital angular momentum of given orbital.

Info F = Radial distance of the spherical node which is farthest from the nucleus (Assuming  $k_3 = 1$ )

Ans. (300303)

**Sol.**  $\Psi_{(r)} = 0$  at radial nodes

$$r^2 - 5k_3r + 6k_3^2 = 0$$

$$k_3 = 1$$
(given)

$$r^2 - 5r + 6 = 0$$

$$\Rightarrow$$
 r = 2,3  $\Rightarrow$  two nodes

Radial node = n - r - 1 = 2

Ψr given is for 'S' orbital

$$n - 0 - 1 = 2$$

$$\Rightarrow 1 = 0$$

$$n = 3$$

$$C = 0$$

∴ A = 3 principal quant no.

So, the orbital is 3s

Orbital angular momnetum =  $L = \sqrt{I(I+1)\frac{h}{2\pi}} = 0$ ,  $\therefore E = 0$ 

Angular nodes: azimuthal quantum number (I) = 0 for 3s,  $\therefore$  B = 0

$$(n + 5)s$$
 to  $(n + 5)p \Rightarrow 8s$  to  $8p$ 

Energy = n + 
$$l \Rightarrow 8 + 0$$
 to  $8 + 1 \Rightarrow 8$  to  $9$ 

7d also has energy n + l = 9

$$\therefore$$
 total 3  $\Rightarrow$  D = 3

F = 0 for 3s spherical node

- 19. In the Bohr's model, for uni-electronic species following symbols are used
  - $r_{n/z} \rightarrow Radius$  of nth orbit with atomic number "z"
  - $U_{n/z} \rightarrow Potential$  energy of electron in nth orbit with atomic number "z"
  - $K_{n/z} \rightarrow Kinetic energy of electron in nth orbit with atomic number "z"$
  - $v_{n/z} \rightarrow Velocity$  of electron in nth orbit with atomic number "z"
  - $T_{n/z} \rightarrow Time$  period of revolution of electron in nth orbit with atomic number "z"

Calculate z in all in cases.

(i) 
$$U_{12}$$
:  $K_{1z} = -8:1$ 

(ii) 
$$r_{1z}$$
:  $r_{21}$  = 1:8

(iii) 
$$v_{1,z}$$
:  $v_{3,1} = 9:1$ 

(iv) 
$$T_{1.2}$$
:  $T_{2.z} = 9:32$ 

Represent your answer as a, b, c, d, where a, b, c and d represent number from 0 to 9. a, b, c and d represent the value of "z" in parts (i), (ii), (iii) & (iv). Suppose your answer is 1, 2, 3 & 4 then the same must be filled in OMR sheet as 1234.00.

#### Ans. (1233)

#### **Sol.** K.En = -(En)

$$K.E_n = -\frac{-PE_n}{2} \Rightarrow E_n = \frac{P.E.}{2} \Rightarrow P.E = 2E_n$$

$$E_n = \frac{-13.6 \times 2^2}{n^2} ev$$

$$U_{1,2}^{P.E.} = 2E_n = 2 \times \frac{(-13.6 \times 2^2)}{1^2} ev \dots (1)$$

$$K_{1,1} = -E_n = \frac{13.6 \times 1^2}{1^2} \dots (2)$$

$$U_{1,2}/K_{1,1} = -8/1 \Rightarrow Z = 1$$

$$r_{12}/r_{21} = ?$$

$$r = \frac{0.53 \times n^2}{7} A^o \Rightarrow z = 2$$

$$r_{12} = \frac{0.53 \times 1^2}{2}, r_{21} = \frac{0.53 \times 2^2}{1}$$

$$r_{12}/r_{21} = \frac{1}{8}$$

$$V_n = 2.18 \times 10^6 \frac{Z}{n} \text{m/s}$$

$$V_{13} = 2.18 \times 10^6 \times \frac{3}{1}$$
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$$V_{3,1} = 2.18 \times 10^6 \times \frac{1}{3}$$

$$\frac{V_{1,3}}{V_{3,1}}\frac{9}{1} \Rightarrow z = 3$$

$$T \propto \frac{n^3}{Z^2}$$

Therefore, 
$$\frac{T_{1,2}}{T_{2,3}} = \frac{{}^{1}\frac{3}{2}{}^{2}}{{}^{2}\frac{3}{3}{}^{2}} = \frac{9}{32} \Rightarrow z = 3$$

∴ 1233 is the answer.

20. When an electron makes transition from (n + 1) state to n state the wavelength of emitted radiations is related to n (n >>>1) according to  $\lambda \propto n^x$ .

What is the value of x?

- (3.00)Ans.
- $\frac{1}{\lambda} = RZ^2 \left( \frac{1}{n^2} \frac{1}{(n+1)^2} \right)$ Sol.

$$\frac{1}{\lambda} = RZ^2 \left( \frac{(n+1)^2 - n^2}{n^2 (n+1)^2} \right)$$

$$\frac{1}{\lambda} = RZ^2 \left( \frac{(n+1+n) - (n+1-n)}{n^2 (n+1)^2} \right)$$

$$\frac{1}{\lambda} = RZ^2 \Biggl( \frac{(2n+1)}{n^2(n+1)^2} \Biggr)$$

$$\lambda \propto n^3$$
  
  $x = 3$ 

21. Match the following.

Column I

- Column II
- (A) The d-orbital which has two angular nodes
- (P)  $3d_{y^2-y^2}$
- (B) The d-orbital with two nodal surfaces form cones (Q) 3d<sub>-2</sub>
- (C) The orbital without angular node
- (R) 4 f
- (D) The orbital which has three angular nodes
- (S)3s
- (A)  $A \rightarrow P$ , R;  $B \rightarrow Q$ ;  $C \rightarrow S$ ;  $D \rightarrow R$
- (B)  $A \rightarrow P$ , Q;  $B \rightarrow Q$ ;  $C \rightarrow S$ , R;  $D \rightarrow R$
- (C)  $A \rightarrow P$ , Q;  $B \rightarrow Q$ ;  $C \rightarrow S$ ;  $D \rightarrow R$
- (D)  $A \rightarrow P$ ;  $B \rightarrow Q$ ;  $C \rightarrow S$ ;  $D \rightarrow R$ , S

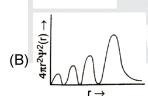
Ans.

- (C)
- Sol. Conceptual
- 22. Match the following.

Column I



(P) 4s



- (Q) 5py
- (C) Angular probability depends upon  $\theta$  and  $\phi$
- (R) 3s
- (D) At least one angular node is present
- (S) 6dxy
- (A)  $A \rightarrow P$ ;  $B \rightarrow P$ ;  $C \rightarrow Q$ , S;  $D \rightarrow Q$ , S
- (B)  $A \rightarrow P$ , Q, S;  $B \rightarrow P$ ;  $C \rightarrow Q$ , S;  $D \rightarrow Q$ , S
- (C) A  $\rightarrow$  P, S; B  $\rightarrow$  P, Q, S; C  $\rightarrow$  Q; D  $\rightarrow$  Q, S
- (D)  $A \rightarrow P$ ;  $B \rightarrow P$ , Q, S;  $C \rightarrow Q$ , S;  $D \rightarrow Q$ , S

Ans. (D)

Sol. Conceptual

#### SUBJECTIVE ANSWER TYPE

- 23. Using Bohr's theory show that when n is very large, the frequency of radiation emitted by hydrogen atom due to transition of electron from n to (n 1) is equal to frequency of revolution of electron in its orbit.
- **Sol.**  $E_n E_{n-1} = hv$ , where v is the frequency of radiation emitted by H-atom due to transition of electron from n to (n-1)

$$\therefore \qquad v = \frac{2\pi^2 m e^4 k^2 z^2}{h^3} \left[ \frac{1}{(n-1)^2} - \frac{1}{n^2} \right]$$

$$v = \frac{2\pi^2 m e^4 k^2 z^2}{h^3} \left\lceil \frac{2n-1}{n^2 (n-1)^2} \right\rceil = \frac{2\pi^2 m e^4 k^2 z^2}{h^3} \left\lceil \frac{2-1/n}{n (n-1)^2} \right\rceil$$

For very large values of n,

$$\therefore v = \frac{4\pi^2 me^4 k^2 z^2}{n^3 h^3} \qquad .....(1)$$

The frequency of revolution of electron in nth orbit,  $f_n$  is given by :

$$f_n = \frac{v_n}{2\pi r_n} = \frac{\frac{2\pi kze^2}{nh}}{\frac{n^2h^2}{4\pi^2me^4zk}} = \frac{4\pi^2me^4k^2z^2}{n^3h^3} = \frac{4\pi^2me^4k^2z^2}{n^3h^3} \dots (2)$$

From (i) & (ii) for very large values of n, the frequency of radiation emitted by H-atom due to transition of electron from n to (n - 1) is equal to frequency of revolution of electron in its orbit.

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