U.G. 1st Semester Examination - 2022

CHEMISTRY

[HONOURS]

Course Code : CHEM-H-CC-T-01

Full Marks : 40 Time : $2\frac{1}{2}$ Hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

GROUP–A

(Inorganic)

[Marks : 20]

1. Answer any **one** question: $1\times1=1$

   a) Show that with increasing the principal quantum number the velocity of an electron decreases.

   b) Give the relation between electron affinity of X(g) atom and ionization potential of X(g) ion.

2. Answer any **two** questions: $2\times2=4$

   a) On the basis of exchange energy explain why $3d^5 4s^1$ electronic configuration is more stable than $3d^4 4s^2$ electronic configuration.

b) Justify: Zr and Hf often coexist in nature and their separation is difficult.

c) Find out the 'ground state term' for a free ion with $3d^7$ configuration.

d) The first electron affinity of oxygen is exothermic but second electron affinity is endothermic. Explain.

3. Answer any **one** question: $5\times1=5$

a) i) State the Slater's rule.

ii) Radii of isoelectric ions O^-, F^-, Na^+, Mg^{2+} are not equal– explain.

iii) Calculate the de-Broglie wavelength of an electron travelling at 10% of the speed of light. Mass of the electron $(m) = 9.1\times10^{-31}$ kg. $1+2+2=5$

b) i) What are 'radial functions' and 'radial distribution functions' of an orbital? Interpret the relative penetrations of 2s and 2p orbitals from their radial distribution plots.

ii) The interatomic distance in chlorine molecule is 1.98 Å. Calculate the Allred-Rochow Electronegativity of chlorine. $3+2=5$

4. Answer any **one** question: $10 \times 1 = 10$

a) i) P, Q, R are the elements of same period in the periodic table. From their 1st and 2nd ionization energy table, identify them as alkali metal, alkaline earth metal and non-metal. Justify your answer.

	P	Q	R	
11	17.4	5.39	6.11	
12	35.0	75.6	11.87	(11,12 in kJ/mole)

ii) The Rydberg constant is a true constant like ideal gas constant– justify.

iii) By Slater's rule, show that when Fe^{2+} is reduced, electron enters in the 3d orbital rather than 4s orbital. (Atomic No. of Fe = 26).

iv) Find out the magnitude of orbital angular momentum of the electron in a d orbital.

v) The electronegativity difference of A and B elements in A-B molecule are 2. What is the percent (%) of ionic character of A-B bond?

vi) Identify the orbital with one radial node and two angular nodes.

$2+2+2+2+1+1=10$

i) Explain the basis of Pauling's electronegativity scale. Calculate the wavelength of β-line in Laymen series of hydrogen atom (Given $R_H = 1.097 \times 10^7$ cm^{-1}).

ii) What does $4\pi r^2 R(r)^2 = 0$ signify? (R and r have their usual significance).

iii) What is Aufbau principle? Explain any two of its exceptions with respect to the electron filling in Lanthanoids.

iv) Discuss the physical significance of magnetic quantum number.

$(2+2)+1+3+2=10$

GROUP–B

(Physical)

[Marks : 20]

5. Answer any **one** question: $1 \times 1 = 1$

a) Define an intensive property.

b) How can a gas above its critical temperature be liquified?

6. Answer any **two** questions: $2 \times 2 = 4$

a) Can van der Waals' equation for a gas be expressed as : $P.y(\bar{V} - b) = RT$? Here P is the

ideal pressure of the gas, $\bar{V}$ is the volume per mole, b is the volume correction term and T is the temperature. If not, why? If yes, when? 2

b) State conditions for which the following equations are valid (any **two**): 1×2

i) $W = -\int PdV$

ii) $PV^{\gamma} = constant$

iii) $dU = C_V\, dT$

c) Roughly sketch the Lennard-Jones potential curve [V(r) versus r plot] and indicate the empirical parameters σ (the collision diameter) and ϵ (the potential - well depth) in it. 2

7. Answer any **one** question: 5×1=5

a) Schematically draw a plot of probability density $\left[\left(\frac{1}{dC}\frac{dn_C}{N}\right)\right]$ versus C, as given by Maxwell-Boltzmann distribution of speeds, where N is the total number of molecules and dn_C is the number of molecules with speed between C to C + dC. Explain the nature of

the curve. What is the total area under the curve? How does the total area depend on temperature? 1+2+1+1=5

b) 2 moles of an ideal gas initially at 2 atm., 600 K undergoes the following cycle of reversible changes:

(2 atm., 600K, 49.23 L) $\rightarrow$ (1.5 atm., T_2, V_2) Step I : isothermal expansion,

(1.5 atm., T_2, V_2) $\rightarrow$ (1 atm., T_3, V_3) Step II : adiabatic expansion,

(1 atm., T_3, V_3) $\rightarrow$ (2 atm., 600K, V_1) Step III: compression

Find the values for V_1, T_2, Heat taken up in step I (Q_1) and ΔU for step III and for the cycle. [$\overline{C_v}$ for the gas is 1.5 R]. 1+1+1+1+1=5

c) i) Calculate the root mean square velocity $\langle c^2 \rangle^{\frac{1}{2}}$, the average velocity $\langle c \rangle$ and the most probable velocity c_p for hydrogen gas at 273 K.

ii) Write a short note on London interaction. 3+2=5

Answer any **one** of **Q. Nos. 8** and **9**: 10×1=10

8. a) What is Joule's experiment ? What conclusion can be drawn with respect to the nature of an ideal gas from this experiment?

b) 5 moles of an ideal gas ($\gamma = 1.4$), initially at 4 atm. pressure and 400K is expanded adiabatically against a constant opposing pressure of 2 atm. to a final state where mechanical equilibrium is established. Calculate the final temperature of the gas and change in internal energy of the gas.

OR

The heat of the reaction : $A_2 + 2B_2 = 2AB_2$ is 200 kJ at 300 K. What is the value of the heat of reaction at 600 K, given that,

$$\overline{C_P}(A_2) = 1.7 - 2\times10^{-3}T + 1.5\times10^{-6}T^2 \text{ J.mol}^{-1}\text{K}^{-1}$$

$$\overline{C_P}(B_2) = 2.7 + 1.2\times10^{-3}T + 3.5\times10^{-6}T^2 \text{ J.mol}^{-1}\text{K}^{-1}$$

$$\overline{C_P}(AB_2) = 6.7 + 8.2\times10^{-3}T + 4.5\times10^{-6}T^2 \text{ J.mol}^{-1}\text{K}^{-1}$$

c) Prove that reversible adiabates involving ideal gas as working substance are steeper than corresponding isotherms.

d) Prove that for a reversible process and an irreversible process between the same initial and final states, if the irreversible process is adiabatic, the corresponding reversible process cannot be adiabatic.

$(1+1)+4+2+2=10$

9. a) Answer any **one**:

i) Should the gas obeying $P(\overline{V} - b) = RT$ liquefy on compression? Justify.

ii) Evaluate the average molecular kinetic energy of molecules for a system which obeys the following speed (C) distribution equation: $\rho(C)=K.e^{-\frac{mc^2}{2kT}}$, where m is the mass of a molecule, T is the temperature.

b) Answer any **two**:

i) What is the reduced mass of CO molecule?

ii) What is the average speed of CO molecule at 300 K and 1 atm. pressure?

iii) Gas viscosity is not due to intermolecular attraction– justify.

iv) The difference between $\overline{C_v}$ values of linear and nonlinear polyatomic (higher than diatomic) molecules is $\frac{1}{2}RT$ – prove.

c) Define Hess's law of constant heat summation. One mole of an ideal gas expands against a constant external pressure of 1 atm from a volume of 60 dm^3 to 90 dm^3. Calculate the work done by the gas in joules at 298 K. (Given: R = 0.082 $dm^3 atm\ K^{-1}\ mol^{-1}$)

2+(1×2)+(2+4)=10