Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
First Semester, 2023-2024

CHEM G553	**Advanced Physical Chemistry**	**Date: 13.12.2023**
Comprehensive Examination (Open Book)	**Time: 120 mins.**	**[50 M]**

Q1. (a) Consider a particle in a cubic box in a state with an energy of $\frac{14}{3}$ times that of the lowest level. What is the degeneracy of the state? **[4]**

(b) An emission line from the first excited state of K atoms is found to have two closely spaced components, one at 766.70 nm and the other at 770.11 nm. Determine the splitting in terms of cm^{-1} and explain the observation in terms of the energy levels. **[3]**

(c) Write the expression for the radial distribution function of a 3s electron in a hydrogen atom of atomic number Z. Determine the number of locations at which the electron is most likely to be found. **[3]**

Q2. (a) The B_0 value of 1.923601 cm^{-1} is obtained from the rotational Raman spectrum of $^{14}N^{15}N$. The r_0 value for $^{14}N_2$ is 1.100105 Å. **[8]**

(i) Calculate the bond length (r_0) for $^{14}N^{15}N$.

(ii) Compare and comment on r_0 values of $^{14}N^{15}N$ and $^{14}N_2$.

(iii) Comment on the r_e values of $^{14}N^{15}N$ and $^{14}N_2$.

(iv) Would there be an intensity alteration in the spectrum of $^{14}N^{15}N$ compared to that of $^{14}N_2$?

(v) What would be the intensity of the rotational spectrum for $^{14}N^{15}N$?

(b) The chemical shift of the CH_3 protons in diethyl ether is $\delta = 1.16$ and that of the CH_2 protons is 3.36. What is the difference in the local magnetic field between the two regions of the molecule in the presence of an applied magnetic field of 20 T? **[2]**

Q3. (a) A sample consisting of 2.0 mol of $CaCO_3(s)$ was heated to 800 °C, when it was decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during the complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere? **[3]**

(b) A sample consisting of 2.0 mol of perfect gas molecules, for which $C_{V,m}$ = (5/2) R, initially at p_1 = 111 kPa and T_1 = 277 K, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU, q, and w. **[3]**

(c) Calculate ΔS for the system when the state of 2.0 mol of diatomic perfect gas molecules is changed from 25 °C and 1.50 atm. to 135 °C and 7.0 atm. **[4]**

Q4. (a) Calculate ΔU, ΔH, ΔS, ΔA, and ΔG for the following change in the state of 2.50 mol of a perfect monoatomic gas with $C_{V,m}$ = (3/2)R for (28.5 L, 400 K $\rightarrow$ 42 L, 400 K). **[5]**

(b) For an ideal gas reaction, A + B $\rightleftharpoons$ C, a mixture with n_A = 1.0 mol, n_B = 3.0 mol, and n_C = 2.0 mol is at equilibrium at 300 K and 1.0 bar. The pressure is isothermally increased to 2.0 bar; find the new equilibrium amounts. **[5]**

Q5. (a) For the mechanism: A + B $\rightarrow$ C + D; 2C $\rightarrow$ F; F + B $\rightarrow$ 2A + G. (i) Write the stoichiometric number of each step and the overall reaction. (ii) Classify each species as reactant, product, intermediate, or catalysis.

(b) The first order reaction 2A $\rightarrow$ 2B + C is 35% complete after 325 s. How long it will take for the reaction to be 70% complete? **[2]**

(c) If the reaction A $\rightarrow$ products is zero-order, sketch [A] versus t with justification. **[3]**

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