1. (a) Derive the energy expression for the particle-in-a-box solution for the case of n = 3.
   (b) Sketch the corresponding wavefunction.
   (c) Obtain the expression for the momentum and show de Broglie wave relation that: $p = h/\lambda$, for the case of n = 3. (8%)

2. (a) Give the three π Hückel MOs for benzene.
   (b) Show they are orthogonal to each other.
   (c) Show the total charge density is the same on each atom. (7%)

3. Experiment shows that the rate of formation of CCl_4 from $CHCl_3$ is first order in $CHCl_3$, 1/2 order in Cl_2, and 3/2 order overall.

$$CHCl_3\,(g) + Cl_2\,(g) \longrightarrow CCl_4\,(g) + HCl\,(g)$$

   (a) Give a possible reaction mechanism consistent with the rate law.
   (b) From (a), give the examples for the terms such as elementary reactions, rate-determining step and reaction intermediate. (10%)

4. A gaseous molecule has two states denoted as A and B. The energy difference between these two states is $\Delta E = E_B - E_A = 1$ kJ mol^{-1}. Estimate the temperature (T) for a sample of this gas when the population ratio of gases in these two states is $n_A/n_B = 10$ at a pressure of 1 bar. (5%)

5. Estimate ΔS, ΔG, ΔU, w and q on expanding one mole ideal gas from $P_i = 10$ bar to $P_f = 1$ bar against an external pressure of $P_{ext} = 0$ at 300 K. (10%)

6. Prove that $K_{eq} = \exp(-\Delta_{rex}G^0)$ for a reaction of A + B = C + D. Please give necessary assumptions. (10%)

7. Express the results of the following calculations using only significant figures. (8%)
   (a) (39.64)(0.1001)(55.85)/(22.272)
   (b) 236.30 + 12.2 – 1.6342

8. The atomic mass of the four most common elements found in organic compounds are $^{12}C = 12.000$; $^{1}H = 1.008$; $^{16}O = 15.995$; $^{14}N = 14.003$. What resolving power of a mass spectrometer would be needed to distinguish between the molecular ions of a mixture of methanol and oxygen? (6 %)

9. In the HPLC determination of the vitamin C and the saccharin content of a soft-drink concentrate, Caffeine was used as the internal standard. A standard solution containing vitamin C (250 ppm w/v), saccharin (100 ppm w/v), and caffeine (150 ppm w/v) was prepared. The corresponding HPLC results show the peak height (cm) of 15.15 (for vitamin C), 10.50 (for saccharine) and 12.25 (for caffeine). 20.0 cm^3 of a soft-drink was pipetted into a 100.0 cm^3 volumetric flask, and to it was added a 5.00 mg of pure caffeine. The mixture in the flask was diluted to volume with distilled water. The corresponding HPLC results show the peak height (cm) of 6.95 (for vitamin C), 5.00 (for saccharine) and 8.30 (for caffeine). Assuming a linear relationship exists between the measured peak height and concentrations for all three components over the concentration range examined, calculate the concentration (mg dm^{-3}) of vitamin C and of saccharin in the soft-drink concentrate. (10 %)

10. Suggest an appropriate HPLC detector for the following analytes. Explain your selection. (12 %)

(a) The determination of vitamin C in a multivitamin.
(b) The separation of polystyrene into fractions of different molecular mass, using size exclusion chromatography.
(c) The determination of phenols as contaminants in a sample of river water.
(d) The determination of vitamin B2 in milk.

11. Why is source modulation employed in atomic absorption spectrometry? (6 %)

12. Briefly describe the means to calibrate a volumetric flask. (8 %)