Birla Institute of Technology & Science, Pilani (Raj)
Pilani Campus
II Semester, 2021-2022
CHEM G554 Physical Methods in Chemistry
Mid Semester Test (Open Book- offline)

Max. Marks: 35 **11 March 2022** **Duration: 1hr 30 min.**

Instructions to the student:

1) There are seven questions in total; answer all the questions.
2) Write brief answers to the point with proper justification.
3) Start answering each question on a fresh page and answer all parts of a question together.
4) Open book test. Textbook, Ref. books, class notes, and printed slides are allowed. However, exchange of these materials is not allowed. Mobile phones, lap-tops etc. are to be switched off and kept away from you.
5) Any unfair means, if identified, will be sternly dealt with.
6) Data required are available in Text and/or Reference books. However, for quick reference the following often used constant values are given.

DATA: **R** = 8.3145 J mol^{-1} K^{-1}; **R**= 0.0820575 L atm K^{-1} mol^{-1}; **k** = 1.38065 x 10^{-23} J K^{-1};
Avogadro's Number = $\mathbf{N_A}$ = 6.022142 x 10^{23} mol^{-1}; **h** = 6.626069 x 10^{-34} J s;
e = 1.60216 x 10^{-19} C; $\mathbf{m_e}$ = 9.10938 x 10^{-31} kg; **F** = 96485.34 C mol^{-1};
c = 2.99792458 x 10^8 m s^{-1}; $\boldsymbol{\varepsilon_0}$ = 8.854188 x 10^{-12} C^2 N^{-1} m^{-2}; **g** = 9.807 m s^{-2}.

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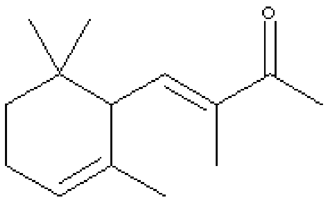
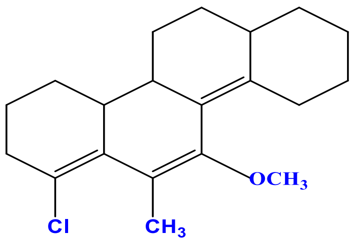
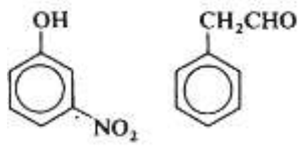
1. a) Express 412 kJ/mol in terms of i) Hz ii) eV **[1]**

b) Explain "natural linewidth". **[1]**

c) Predict the λ_{max} for $\pi \rightarrow \pi^*$ transition (based on Woodward Rules) for the following species (i and ii) in cyclohexane and hexane solutions respectively. **[3]**

(i)  **(ii)** 

2. a) For each of the following molecules, state the number and relative intensities of the carbon 1s ESCA peaks and do the same for the oxygen 1s ESCA peaks. **[2]**



b) For the molecular formulas $C_{12}H_{10}$ and $C_{11}H_{16}$ calculate the double bond equivalence and write a structure for each case that is consistent with the calculated DBE. **[2]**

c) A component called "chopper" is used in some spectrometers. This component periodically switches off and on the EMR falling on the sample (say 50 times/ sec). Can you visualize for what purpose this hardware component is used in spectrometers? **[1]**

3. a) Ethyl bromide shows proton NMR signals at (δ =) 1.8 and 3.5 ppm. The coupling constant is 8 Hz. (a) What will be the exact frequencies of the three peaks in the triplet in an 80 MHz NMR spectrometer? (b) What will be the exact frequencies of the four peaks in the quartet in a 400 MHz NMR spectrometer? **[2 + 2 = 4]**

b) A 90 MHz NMR spectrometer is used to record the signals of protons at a magnetic field of 21140 G. With the same magnet, if ^{13}C NMR is to be recorded, what should be the frequency of EMR used (approximately)? **[1]**

P.T.O.

4. a) What will be the symmetry species of the state that results from (i) $n \rightarrow \sigma^*$ (ii) $\pi \rightarrow \pi^*$ transitions in formaldehyde? **[2]**
b) How will you distinguish 2-methylcyclohexanone from 3-methylcyclohexanone by using ORD? In both the species methyl group is in axial position. **[3]**

5. Predict the proton NMR chemical shift positions for the following compounds **a)** phenacetin (p-$CH_3CH_2OC_6H_4NHCOCH_3$) **b)** methyl benzoate **c)** p-hydroxybenzaldehyde **d)** o-dihydroxy benzene **e)** paracetamol ($HOC_6H_4NHCOCH_3$) **[5]**

6. a) Consider AX spin coupled systems. Write the different spin combinations and arrange them energy wise before coupling. In the same diagram indicate what happens to the energy levels after coupling **a)** with positive coupling constant and **b)** with negative coupling constant. **[3]**
b) The fluorescence life time in the absence of a quencher is 1.4 ns and in the presence of a quencher it is 0.8 ns. Calculate the quenching efficiency, which is the ratio of the quantum yields in the presence and absence of the quencher. **[2]**

7. Given below is the proton NMR spectrum of a hydrocarbon (C_9H_{12}) recorded at 60 MHz. The integration (area under the curve) values are: the peak at δ = 7.3 (5 units); the multiplet (1 unit) ; peaks near δ = 1.2 and 1.4 (3 units each). Deduce the structure of the compound. **[5]**