

**Tutorial Problem Set 3 (based on Lecture No.'s: 17-21 in the course hand out)**

**Instructions to the student:** *The following problems should be solved as home assignment within a week of display. One or more problems will be assigned as a closed book class test in the following tutorial hour.*

Q1. (a) What can be the value of  $\delta$  for a nucleus in a spectrometer operating at 200 MHz, if it has a resonance frequency of 300 MHz.

(b) For the HNMR spectrum of the following compounds, predict: (i) the no. of signals and (ii) the position of the signals relative to each other:

(i) Ethyl chloride, (ii) Isopropyl chloride, (iii) 1-chloropropane. [4 + 2 × 3]

Q2. (a) State the total no. of signals that will be observed in the  $^{13}\text{C}$  NMR spectrum of the following compounds. Also label the different carbons that would give rise to those signals.

(i) Methylcyclopentane, (ii) 2-Methylbut-2-ene [5]

(b) What magnetic field strength is required for proton magnetic resonance at 220 MHz. Given g factor for proton is 5.585 and the nuclear magneton ( $\mu_n$ ) is  $5.047 \times 10^{-27} \text{ J Tesla}^{-1}$ . [5]

Q3. (a) The HNMR spectrum of a compound  $\text{C}_3\text{H}_5\text{ON}$  shows the following absorptions:  $\delta$  2.1 (brs, 1H);  $\delta$  2.5 (triplet, 2H);  $\delta$  3.9 (triplet, 2H). Predict the structure and state which peak is due to which set of protons. [5]

(b) Given the following compound:  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{Br}$ . Answer the following questions pertaining to its  $^1\text{H}$ NMR spectrum: (a) How many signals will be observed in its  $^1\text{H}$ NMR spectrum? (b) What will be the multiplicity of each signal? (c) Which set of protons will appear most downfield? [5]

Q4. (a) A chemical reaction takes place in a container of cross-sectional area  $50.0 \text{ cm}^2$ . As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system. [4]

(b) One mol of an ideal gas in an isolated system expands freely from 28.0 L at 400 K to 42.0 L at 400 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surroundings}}$  and  $\Delta S_{\text{universe}}$ . Show that the results are in accordance with the second law of thermodynamics. (Hint: Free expansion of a gas is an irreversible process).  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ . [6]

Q5. A sample consisting of 2.00 mol of He (assumed to behave ideally) is expanded isothermally at  $22^\circ\text{C}$  from  $22.8 \text{ dm}^3$  to  $31.7 \text{ dm}^3$ , (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w,  $\Delta u$ , and  $\Delta H$ . [10]

Q6. (a) A piece of Zinc of mass 5.0 gm is placed in a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and temperature is  $23^\circ\text{C}$ . [8]

(b) Given that the standard enthalpy of combustion of graphite is  $-393.51 \text{ kJ mol}^{-1}$  and that of diamond is  $-395.41 \text{ kJ mol}^{-1}$ , calculate the enthalpy of the graphite-to-diamond transition [2]

Q7. (a) Calculate  $\Delta H$  and  $\Delta G$  when 2 mol of an ideal gas expands isothermally and reversibly from 30.0 L to 45.0 L at 300 K.  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ . [5]

(b) How much glucose does a person of mass 60 kg need to consume to climb through 10 m? Given that, the change in Gibbs energy that accompanies the oxidation of 1.0 mol of  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$  to carbon dioxide and water vapour at  $25^\circ\text{C}$  is  $-2828 \text{ kJ}$ .  $g = 9.81 \text{ ms}^{-2}$ ,  $M_{\text{C}_6\text{H}_{12}\text{O}_6} = 180 \text{ g mol}^{-1}$ . [5]

Q8. (a) Calculate  $\Delta_r S^\circ$  for the reaction,  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$ . Given that,  $S_m^\circ(\text{H}_2, \text{g}) = 131 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S_m^\circ(\text{O}_2, \text{g}) = 205 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $S_m^\circ(\text{H}_2\text{O}, \text{l}) = 70 \text{ J K}^{-1} \text{ mol}^{-1}$ . For this reaction,  $\Delta_r H^\circ = -572 \text{ kJ mol}^{-1}$ .

Calculate  $\Delta S_{\text{surroundings}}$ . Show that the results obtained are in accordance with the second law of thermodynamics.

[6]

(b) . Calculate  $\Delta H$  and  $\Delta G$  for the melting of 1 mol of ice at  $0^{\circ}\text{C}$  and 1 atm. Given that, latent heat of fusion of ice at  $0^{\circ}\text{C}$  and 1 atm is  $333 \text{ J g}^{-1}$ . How does the result obtained make sense?

[4]

Q9. (a) A compound having molecular formula  $\text{C}_8\text{H}_{10}\text{O}_2$  shows the following spectral data:

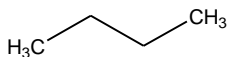
$^1\text{H NMR}$ :  $\delta$  7.0 (doublet, 2H);  $\delta$  6.8 (doublet, 2H);  $\delta$  4.8 (broad singlet, 1H);  $\delta$  3.9 (quartet, 2H);  $\delta$  1.4 (triplet, 3H). IR (important peaks):  $3300 \text{ cm}^{-1}$  (broad);  $1100 \text{ cm}^{-1}$  (strong). Predict the structure of the compound and state which NMR peak is due to which set of protons.

[6]

(b) How many  $^1\text{H NMR}$  signals would you expect from each of the following compounds? Label each set of protons clearly by drawing structures

[4]

(i)



(ii)

