1. (Total 12 pts) The following reaction occurs in an electrochemical cell (25 °C).

$$3HClO_{2(aq)} + 2Cr^{3+}_{(aq)} + 12H_2O_{(l)} \rightarrow 3HClO_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 8H_3O^+_{(aq)}$$

(a) Calculate E° for this cell.

(b) Calculate ΔG° for this cell.

(c) Calculate the equilibrium constant for this reaction.

(d) At pH 0, with $[Cr_2O_7^{2-}] = 0.8$ M and $[HClO_2] = 0.15$ M, and $[HClO] = 0.2$ M, the cell potential is found to equal 0.15 V. Calculate the concentration of $Cr^{3+}_{(aq)}$ in the cell.

2. (Total 14 pts) Consider the electrolysis of pure water.

$$H_2O \rightarrow H_2 + 1/2O_2$$

(a) Write the half-cell reactions for the cathode and anode.

(b) Assuming that the hydrogen and oxygen are produced at atmospheric pressure, calculate the reduction potential for each half-reaction at pH = 7.

(c) What is the overall cell potential? Is the reaction spontaneous? How much potential should be applied for the electrolysis of pure water to occur?

(d) Suppose you apply 1.5 V on 0.1 M aqueous solution of NaCl. Which substances will be generated in the cathode and in the anode, respectively? (Rationalize your explanation based on the analysis of the reduction potential of each substance present in the solution.)

3. (Total 6 pts) Iodine atoms combine to form molecular iodine in the gas phase :

$$I_{(g)} + I_{(g)} \rightarrow I_{2(g)}$$

This reaction follows second-order kinetics with $k = 7.0 \times 10^9\ M^{-1}\ s^{-1}$ at 23 °C.

(a) If the initial concentration of I was 0.086 M, calculate the concentration after 2 min.

(b) Calculate the half-life of the reaction if the initial concentration of I is 0.6 M and if it is 0.42 M.

4. (Total 9 pts) The rate constant of the first-order reaction $2N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2(g)}$ is $0.76\ s^{-1}$ at 1000 K and $0.87\ s^{-1}$ at 1030 K.

(a) Calculate the activation energy (E_a) of the reaction.

(b) Calculate the pre-exponential factor (A, from the Arrhenius equation) of the reaction.

(c) What would be the predicted rate constant at 1100 K?

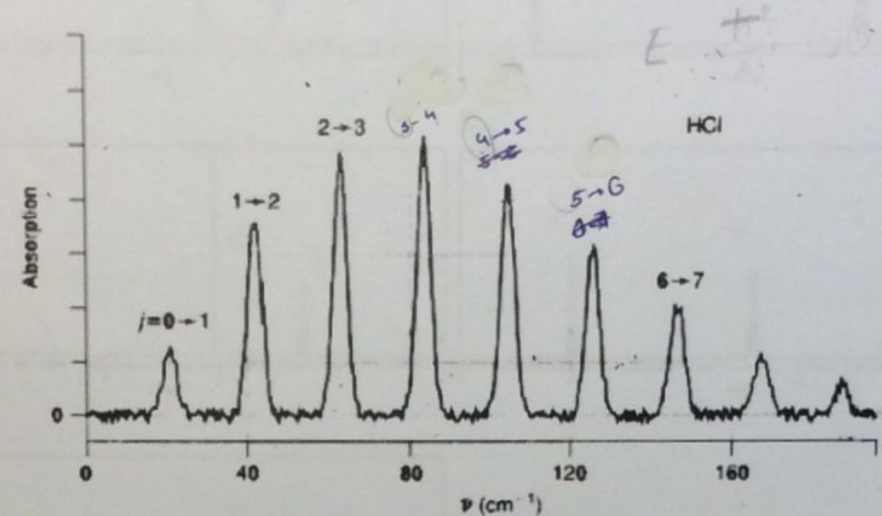
5. (Total 8 pts) The conversion of dissolved carbon dioxide in blood to HCO^{3-} and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 8\times10^{-5}\ molL^{-1}$ and $k_2 = 6\times10^5\ s^{-1}$.

(a) What is the maximum rate of reaction of carbon dioxide if the enzyme concentration is 5×10^{-6} M?

(b) At what CO^2 concentration will the rate of decomposition be 30% of that calculated in part (a)?

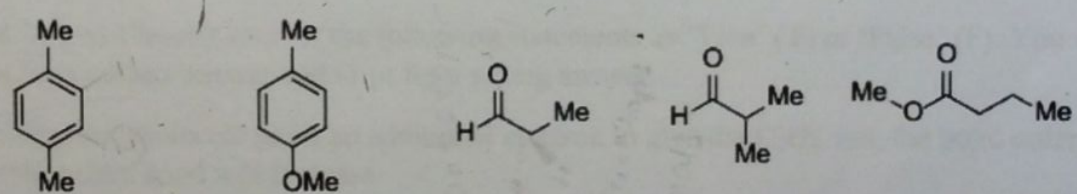
6. (7 pts) Following figure is a pure rotational spectrum for HCl. The line positions of the fourth, fifth, and sixth lines of the spectrum shown in the figure are $\tilde{\nu}_4 = 83.03\ \text{cm}^{-1}$, $\tilde{\nu}_5 = 103.8\ \text{cm}^{-1}$, and $\tilde{\nu}_6 = 124.3\ \text{cm}^{-1}$. Find the equilibrium bond length r_e for HCl. Note that $\tilde{B} = \left(\frac{h}{8\pi^2 cI}\right)$.

($m_H = 1.00$, $m_{Cl} = 35.00$)



7. (Total 12 pts)

(a) Predict the number of peaks (set of peaks generated by spin-spin coupling is counted as one peak) in the proton NMR spectrum of the following compounds.



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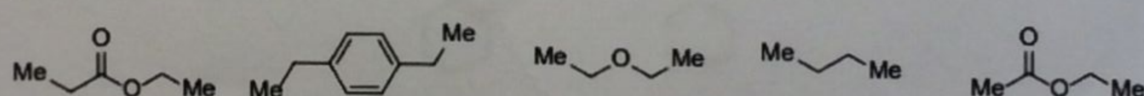
(b) Below are the ^{1}H NMR spectra (DMSO-d_6, 300 MHz) of five different compounds. Assign the spectra to each compounds. Refer the ^{1}H NMR chemical shift chart.



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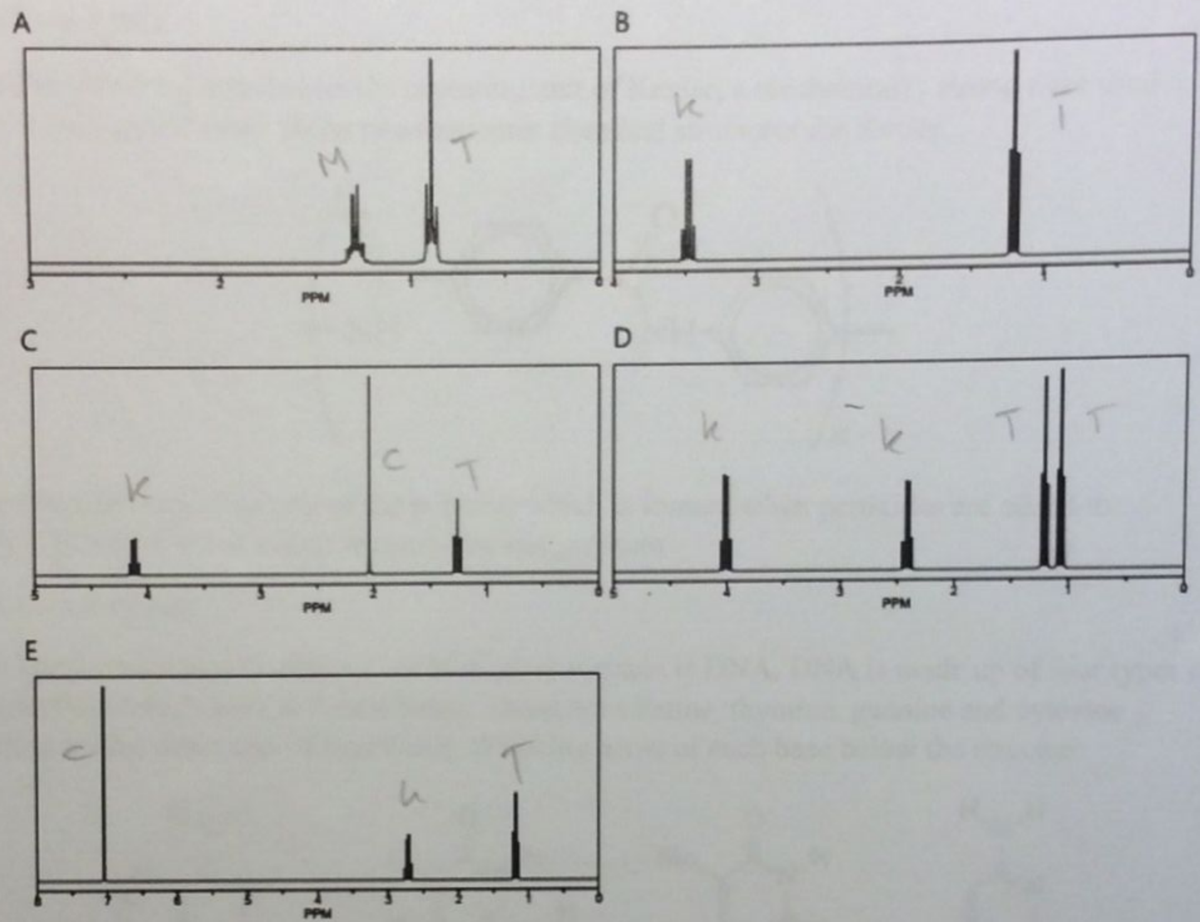
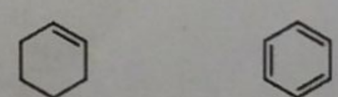


8. (Total 14 pts) Classify each of the following statements as 'True' (T) or 'False' (F). You will get 2 pts for a correct answer and -1 pt for a wrong answer.

(a) If an ethylene molecule gains an additional electron to give the $C_2H_4^-$ ion, the bond order of the carbon-carbon bond will increase.

(b) If an electron in the π orbital of C_2H_4 is excited by a photon to the π^* orbital, the vibrational frequency in the excited state will be higher than in the ground state.

(c) The structure of the molecules cyclohexene and benzene are shown below.



cyclohexene   benzene

The absorption of ultraviolet light by benzene occurs at shorter wavelength.

(d) Intersystem crossing is enhanced between states of different orbital configurations for organic molecules containing only the lighter elements.

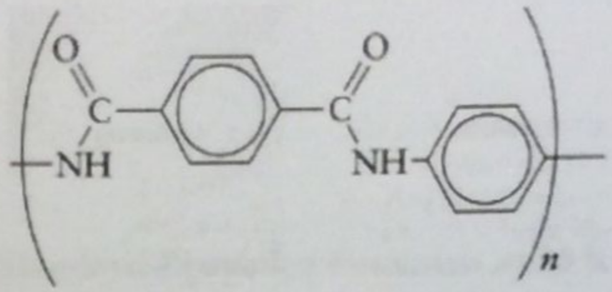
(e) Φ_p's are small for molecules that have rapid $S_1 \rightarrow T_n$ intersystem crossing rates.

(f) Bacteria have a single photosynthetic system that absorbs longer wavelengths than plants and does not produce holes sufficiently oxidizing to oxidize water.

(g) A strong absorption observed in the ultraviolet region of the spectrum of formaldehyde is attributed to an $n \rightarrow \pi^*$ transition.

9. (Total 8 pts)

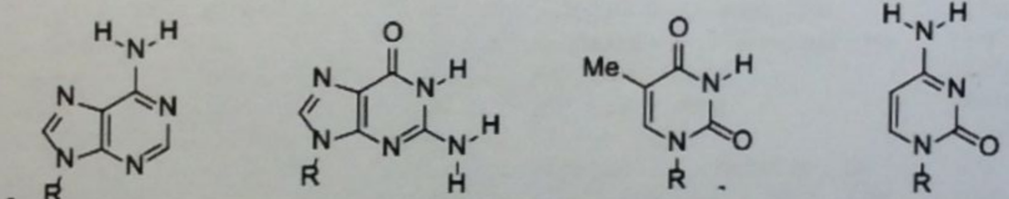
(a) The following structure is the repeating unit of Kevlar, a mechanically strong fiber used to make bulletproof vests. Draw two monomer chemical structures for Kevlar.



(b) Draw the repeating unit of the polymer which is formed when peroxides are added to CH3CH2CH=CH2 at a high temperature and pressure.

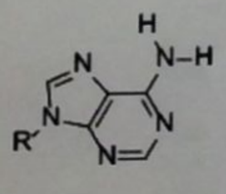
10. (Total 10 pts)

(a) The primary genetic material of biological systems is DNA. DNA is made up of four types of nucleotides which have different bases. Those are adenine, thymine, guanine and cytosine. Below are the structures of four bases. Write the name of each base below the structure.



adenine . Guanine Thymine Cytosine

(b) Adenine and thymine can form two intermolecular hydrogen bonding which enable the formation of DNA double helix. Indicate these two hydrogen bonds from the molecular structure of these two bases.



adenine thymine

(c) Guanine and cytosine can form three intermolecular hydrogen bonding which enable the formation of DNA double helix. Indicate these three hydrogen bonds from the molecular structure of these two bases.

guanine cytosine

<Standard Reduction Potentials at 25 °C>

Half-Reaction	E° (volts)
$F_2(g) + 2e^- \rightarrow 2F^-$	2.87
$H_2O_2 + 2H_3O^+ + 2e^- \rightarrow 4H_2O$	1.776
$Au^+ + e^- \rightarrow Au(s)$	1.68
$MnO_4^- + 4H_3O^+ + 3e^- \rightarrow MnO_2(s) + 6H_2O$	1.679
$HClO_2 + 2H_3O^+ + 2e^- \rightarrow HClO + 3H_2O$	1.64
$HClO + H_3O^+ + e^- \rightarrow Cl_2(g) + 2H_2O$	1.63
$Ce^{4+} + e^- \rightarrow Ce^{3+}$ (1 M HNO_3 solution)	1.61
$2NO(g) + 2H_3O^+ + 2e^- \rightarrow N_2O(g) + 3H_2O$	1.59
$BrO_3^- + 6H_3O^+ + 5e^- \rightarrow Br_2(\ell) + 9H_2O$	1.52
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	1.51
$MnO_4^- + 8H_3O^+ + 5e^- \rightarrow Mn^{2+} + 12H_2O$	1.491
$ClO_3^- + 6H_3O^+ + 5e^- \rightarrow Cl_2(g) + 9H_2O$	1.47
$PbO_2(s) + 4H_3O^+ + 2e^- \rightarrow Pb^{2+} + 6H_2O$	1.46
$Au^{3+} + 3e^- \rightarrow Au(s)$	1.42
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.3583
$Cr_2O_7^{2-} + 14H_3O^+ + 6e^- \rightarrow 2Cr^{3+} + 21H_2O$	1.33
$O_3(g) + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	1.24
$O_2(g) + 4H_3O^+ + 4e^- \rightarrow 6H_2O$	1.229
$MnO_2(s) + 4H_3O^+ + 2e^- \rightarrow Mn^{2+} + 6H_2O$	1.208
$ClO_4^- + 2H_3O^+ + 2e^- \rightarrow ClO_3^- + 3H_2O$	1.19
$Br_2(\ell) + 2e^- \rightarrow 2Br^-$	1.065
$NO_3^- + 4H_3O^+ + 3e^- \rightarrow NO(g) + 6H_2O$	0.96
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.905
$Ag^+ + e^- \rightarrow Ag(s)$	0.7996
$Hg_2^{2+} + 2e^- \rightarrow 2Hg(\ell)$	0.7961
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.770
$O_2(g) + 2H_3O^+ + 2e^- \rightarrow H_2O_2 + 2H_2O$	0.682
$BrO_3^- + 3H_2O + 6e^- \rightarrow Br^- + 6OH^-$	0.61
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-$	0.588
$I_2(s) + 2e^- \rightarrow 2I^-$	0.535
$Cu^+ + e^- \rightarrow Cu(s)$	0.522
$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-$	0.401
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.3402
$PbO_2(s) + H_2O + 2e^- \rightarrow PbO(s) + 2OH^-$	0.28
$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(\ell) + 2Cl^-$	0.2682
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	0.2223
$SO_4^{2-} + 4H_3O^+ + 2e^- \rightarrow H_2SO_3 + 5H_2O$	0.20

Half-Reaction	E° (volts)
$Cu^{2+} + e^- \rightarrow Cu^+$	0.158
$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	0.0895
$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	0.01
$2H_3O^+ + 2e^- \rightarrow H_2(g) + 2H_2O(\ell)$	0.000 exactly
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	−0.1263
$Sn^{2+} + 2e^- \rightarrow Sn(s)$	−0.1364
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	−0.23
$Co^{2+} + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$	−0.356
$Mn(OH)_3(s) + e^- \rightarrow Mn(OH)_2(s) + OH^-$	−0.40
$Cd^{2+} + 2e^- \rightarrow Cd(s)$	−0.4026
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	−0.409
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.424
$Fe(OH)_3(s) + e^- \rightarrow Fe(OH)_2(s) + OH^-$	−0.56
$PbO(s) + H_2O + 2e^- \rightarrow Pb(s) + 2OH^-$	−0.576
$2SO_3^{2-} + 3H_2O + 4e^- \rightarrow S_2O_3^{2-} + 6OH^-$	−0.58
$Ni(OH)_2(s) + 2e^- \rightarrow Ni(s) + 2OH^-$	−0.66
$Co(OH)_2(s) + 2e^- \rightarrow Co(s) + 2OH^-$	−0.73
$Cr^{3+} + 3e^- \rightarrow Cr(s)$	−0.74
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	−0.7628
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$	−0.8277
$Cr^{2+} + 2e^- \rightarrow Cr(s)$	−0.905
$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	−0.92
$Mn^{2+} + 2e^- \rightarrow Mn(s)$	−1.029
$Mn(OH)_2(s) + 2e^- \rightarrow Mn(s) + 2OH^-$	−1.47
$Al^{3+} + 3e^- \rightarrow Al(s)$	−1.706
$Sc^{3+} + 3e^- \rightarrow Sc(s)$	−2.08
$Ce^{3+} + 3e^- \rightarrow Ce(s)$	−2.335
$La^{3+} + 3e^- \rightarrow La(s)$	−2.37
$Mg^{2+} + 2e^- \rightarrow Mg(s)$	−2.375
$Mg(OH)_2(s) + 2e^- \rightarrow Mg(s) + 2OH^-$	−2.69
$Na^+ + e^- \rightarrow Na(s)$	−2.7109
$Ca^{2+} + 2e^- \rightarrow Ca(s)$	−2.76
$Ba^{2+} + 2e^- \rightarrow Ba(s)$	−2.90
$K^+ + e^- \rightarrow K(s)$	−2.925
$Li^+ + e^- \rightarrow Li(s)$	−3.045