## 物理化學

1. Short questions

   a. Please briefly explain the first law and the second law of thermodynamics. (2pts)

   b. Which of the following transitions: $1s \rightarrow 2s$, $2s \rightarrow 2p$, $1s \rightarrow 3p$, $4s \rightarrow 5d$, are allowed in a hydrogen atom? (2pts)

   c. Please determine the vibrational degrees of freedom in the following molecules: $SF_6$, Benzene, $CH_3Cl$. (3pts)

   d. Please explain the difference between $T_1$ (spin-lattice relaxation time) and $T_2$ (spin-spin relaxation time) in NMR spectroscopy. (2pts).

   e. For a $^1H$ nucleus in a magnetic field of 5 Tesla, what is its Larmor frequency?　What is the Larmor frequency for a $^{13}C$ nucleus in the same magnetic field?　Electron g factor $g_e$= 2.002322, Proton g factor $g_N$=5.585486, Magnetogyric ratio: proton $26.75 \times 10^7$ $T^{-1}$ $s^{-1}$, $^{13}C$ nucleus $6.73 \times 10^7$ $T^{-1}$ $s^{-1}$ (4pts)

   f. Please explain the Steady State Approximation in chemical kinetics. (1pt)

   g. For a first order reaction, what is the relation between half-life time ($t_{1/2}$) and rate constant ($k$)? (1pt)

2. Please estimate the difference between $C_p$ and $C_v$ for $CCl_4$ at 298K, for which $C_p$=132 J $K^{-1}$ $Mol^{-1}$.　At this temperature its density is 1.59 g/cm$^3$, its expansion coefficient ($\alpha$) is $1.24 \times 10^{-3}$ $K^{-1}$, and its isothermal compressibility ($\kappa_T$) is $9.05 \times 10^{-5}$ atm$^{-1}$. (10pts)

3. At 1 atm, the vaporization of $H_2O$: $\Delta H_{vap}$=43.54 kJ $Mol^{-1}$ (298K), $\Delta H_{vap}$=40.68 kJ $Mol^{-1}$ (373K), $C_p$ of $H_2O_{(l)}$ is 75.3 J $K^{-1}$ $Mol^{-1}$

   a. What is the $C_p$ of $H_2O_{(g)}$? (3pts)

   b. What is the $\Delta S$ of $H_2O_{(g)} \leftrightarrow H_2O_{(l)}$ at 373K? (2pts)

4. Hydrogen atomic orbital: $\Psi_{2s} = \dfrac{1}{2\sqrt{2a_0^3}}(2 - \dfrac{r}{a_0})e^{-\frac{r}{2a_0}}$ , $a_0 = 0.529177 \times 10^{-10} m$ , Rydberg constant

   $R_H = 109737 cm^{-1}$

   a. Please find the node and maximum probability positions of the $2s$ orbital of hydrogen atom. (4pts)

   b. Determine the potential energy, $\langle \hat{V} \rangle$, for the $3p_z$ orbital of H atom. (Hint: the virial theorem) (4pts)

   c. What is the wavelength for the $2s \rightarrow 3p$ transition? (2pts)

5. In the low resolution mid-IR spectrum of $H^{35}Cl$, three transitions at 2885.64 cm$^{-1}$, 2781.54 cm$^{-1}$, and 5667.18 cm$^{-1}$, were observed.

   a. Please give the assignments for these three transitions. (5pts)

   b. Please determine the values of vibrational frequency ($\omega_e$) and anharmonicity constant ($\omega_e x_e$) for $H^{35}Cl$. (5pts)

注意：背面有試題

分析化學

6. A compound gives a polarographic wave with $E_{1/2}$ = -0.265V (versus S.C.E.) in 0.05M $H_2SO_4$. A 50.0mL sample containing this compound gave a wave height of 0.37μA. When 2.00mL of 3.00 mM of this compound was added to the sample, the wave height increased to 0.8μA. Find the molarity of this compound in the unknown. (10pts)

7. Draw the electrical circuit for a system of controlled-potential electrolysis with the electrodes, an ammeter, and a voltmeter clearly labeled and lines to connect all the devices. The electron flow direction can be indicated by arrows. What would happen if the electrolysis is performed using a two-electrode cell? (10pts)

8. In FT-IR spectrometry, an interferometer is used to produce an interferogram of which the frequency is much lower than the original optical frequency but still maintains the proportionality. What is the benefit of such a linear reduction in frequency from detection point of view? (10pts)

9. A group of organic pollutants have been extracted from a soil sample ready to be analyzed for their composition. The concentrations of these compounds are at ppm (mg/L) level. What types of instrumentation would you use to perform such an analytical task in order to know their exact concentrations and chemical identities? Explain. (10pts)

10. Which of the following statements regarding the potentiometry or potentiometric redox titration are **false**? (Note: Could be more than one answers.) (10pts)
    (a) It is the cell potential that is being measured.
    (b) It needs a reference electrode and an indicator electrode.
    (c) It is the current that often needs to be measured.
    (d) The internal resistance of the cell is very small to permit large current flowing through the circuit.
    (e) The reduction potential ($E_{reduction}$) for all half reactions in the same beaker are equal at any time, but keep changing as titration continues.