物理化學 Physical Chemistry

1. Short questions

   a. What is the point group symmetry of NH_3? (2pts)

   b. Does the CO_2 molecule have any pure rotational spectrum in microwave region? (2pts)

   c. What is the number of vibrational degrees of freedom for benzene? (2pts)

   d. Please briefly describe the Born-Oppenheimer Approximation. (2pts)

   e. Please briefly describe the Franck-Condon principle. (2pts)

2. For the O atom with $[He]2s^2 2p^4$ electronic configuration, please write down all of the atomic term symbols (including multiplicity, total angular momentum) corresponding to this configuration and determine which term symbol has the lowest energy. (8pts)

3. A series of line in the spectrum of atomic hydrogen lie at 656.46nm, 486.27nm, 434.17nm, and 410.29nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of these transitions? (Rydberg constant for H atom = $109677 cm^{-1}$, speed of light $c = 2.9979 \times 10^8$ m/sec) (10pts)

4. There is a reaction: $2NO + O_2 \rightarrow 2NO_2$. The mechanism is as follows: $2NO \leftrightarrow N_2O_2$ (Rate Constant: $k_1 \rightarrow$, $k_{-1} \leftarrow$), $N_2O_2 + O_2 \rightarrow 2NO_2$ (Rate Constant: k_2). If the first step is a fast equilibrium and the second step is a slow reaction, please use Steady State Approximation to show that $Rate = \left(\dfrac{k_1 k_2}{k_{-1}}\right)[NO]^2[O_2]$. (6pts)

5. Elemental sulfur can exist in two crystalline forms, rhombic and monoclinic. Calculate the temperature for the conversion of monoclinic sulfur to rhombic sulfur given the following data. (6pts)

	ΔH_f^0 (kJ Mol^{-1})	ΔS_f^0 (J K^{-1} Mol^{-1})
S (rhombic)	0	31.88
S (monoclinic)	0.30	32.55

5. If a gas engine operates with 1 mole ideal gas in the following cycle: State (a)→(b) isobaric process, State (b)→(c) isochoric process, State (c)→(a) isothermal process. Let's suppose every step is reversible. If P_a=6atm, V_a=4L, P_b=6atm, V_b=6L, and P_c=4atm, V_c=6L.

   a. Please write down the values of ΔE(change of energy), q(heat), and w(work) of each step. (Define: $\Delta E = q - w$, ln2=0.6931, ln3=1.0986, ln5=1.6094). (6pts)

   b. Please prove that for the whole cycle $\Delta S = 0$. (4pts)

分析化學 Analytical Chemistry (10pts for each question)

7. When given an unknown solution containing heavy metal cations at μg/L level, which are environmentally hazardous and needed to be precisely and accurately determined. Which of the following techniques can provide both quantitative and qualitative results? **Explain why?** (select only one answer with your explanation).

   (a) FT-IR

   (b) GC/MS

   (c) Stripping analysis in voltammetry

   (d) AAS or AES

   (e) HPLC with UV detector

8. How will you detect or reduce systematic errors for a newly developed analytical method? (Note: Could be **more than one** answers.)

   (a) Compare with a different but well-tested method.

   (b) Analyze samples of known composition, such as a Standard Reference Material.

   (c) Analyze a standard repeatedly to calculate its standard deviation.

   (d) Analyze blank samples containing none of the analyte being sought.

   (e) Use standard addition method to correct for the instrumental drift.

   (f) Use internal standard to reduce the matrix effect.

9. Which of the following statements regarding the potentiometry or potentiometric redox titration are **false**? (Note: Could be **more than one** answers.)

   (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.

10. Which of the following statements regarding polarography are true? (Note: Could be **more than one** answers.)

    (a) We measure the current between the Hg working electrode and an inert auxiliary electrode.

    (b) Voltage is measured between the Hg electrode and a reference electrode.

    (c) Much smaller overpotential for H^+ reduction at the Hg electrode surface than Pt or Au surface, which considered as an advantage in polarograpy.

    (d) Much larger overpotential for H^+ reduction at the Hg electrode surface than Pt or Au electrode, which considered as an advantage in polargraphy.

    (e) The limiting current determined from a polarogram is propotional to the analyte's concentraion.

    (f) The half-wave potential ($E_{1/2}$) is compound dependent.

11. An unknown sample was repeatedly measured 5 times, and one of the 5 data points was obviously more distant from the median value than the other 4. Which of the following steps should be taken as to whether to drop or keep this suspicious data point?

    (a) To be safe, drop this suspicious data point and keep the remaining 4, since it looks suspicious.

    (b) Check your notebook to see if an obvious mistake has been recorded and documented, if yes then drop this data point.

    (c) Repeat the measurement to acquire more data points when situation allows.

    (d) Do Q test if no other information can be gained.

    (e) Do F test instead.

    (f) No data points should be omitted.