Part I: Inorganic Chemistry (total points: 50)

(1) (a) Consider the four H1*s* orbitals of CH_4. Find matrix representatives for the operations C_3^+ and S_4^+.(5%)

(b) Confirm that the matrix representatives found in (a) satisfy the group multiplication property. (5%)

(2) The algebraic forms of the f orbitals are a radical function multiplied by one of the factors

(i) $z(5z^2 - 3r^2)$ (ii) $y(5y^2 - 3r^2)$ (iii) $x(5x^2 - 3r^2)$ (iv) $z(x^2 - y^2)$ (v) $y(x^2 - z^2)$

(vi) $x(z^2 - y^2)$ (vii) xyz

Identify the irreducible representations spanned by these orbitals in (a) $\boldsymbol{C_{2v}}$ and (b) $\boldsymbol{T_d}$. (10%)

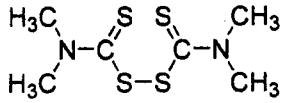
(3) Predict the products of the reactions (there may be more than one product when there are conflicting preferences): (10%)

$PtCl_3NH_3^- + NO_2^- \rightarrow$ (a) (a) + $NO_2^- \rightarrow$ (b)

$PtCl_4^- + I^- \rightarrow$ (c) (c) + $I^- \rightarrow$ (d)

$PtI_4^- + Cl^- \rightarrow$ (e) (e) + $Cl^- \rightarrow$ (f)

(4) $[(C_5H_5)Mo(CO)_3]_2$ reacts with tetramethylthiuramdisulfide (tds), in refluxing toluene to give a molybdenum-containing product having the following characteristics. What is the most likely identity of this product? (10%)

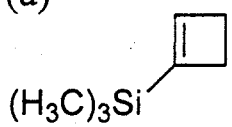


tds

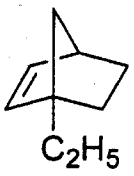
^{1}H NMR: Two singlets, at δ 5.48 ppm (relative area = 5) and δ 3.18 ppm (relative area = 6). (For comparison, $[(C_5H_5)Mo(CO)_3]_2$ has a single ^{1}H NMR peak at δ 5.30 ppm.
IR: Strong bands at 1950 and 1860 cm^{-1}.
Mass spectrum: A pattern similar to the Mo isotope pattern with the most intense peak at *m/e* = 339. (The most abundant Mo isotope is ^{98}Mo.)

(5) Predict the structure of the polymers formed by ring-opening metathesis polymerization. (10%)

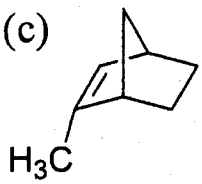
(a)



(b)



(c)



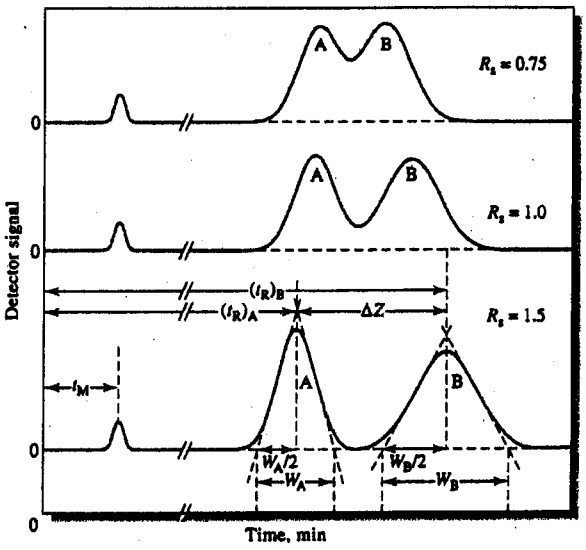
(背面仍有題目,請繼續作答)

Part II: Analytical Chemistry (Total points: 50)

(1) Chemical analyses are affected by chemical and instrumental noises; the later includes (i) Johnson noise, (ii) shot noise, (iii) flicker noise, and (iv) environmental noise.
  (a) Briefly explain what is Johnson noise? (4%)
  (b) What types of instrumental noise are frequency dependent? Frequency independent? (3%)
  (c) Name the type or types of noise than can reduced by (3%)
    (i) decreasing the temperature of a measurement.
    (ii) decreasing the frequency used for the measurement.
    (iii) decreasing the bandwidths of the measurement.

(2) A measurement with a signal-to-noise (S/N) ratio of 100/1 can be thought of as a signal, S, with 1% uncertainty, e, That is, the measurement is $S \pm e = 100 \pm 1$.
  (a) Use the rules for propagation of uncertainty to show that, if you add two such signals, the results is total signal = $200 \pm \sqrt{2}$, given a S/N ratio of $200/\sqrt{2} = 141/1$. (5%)
  (b) Show that averaging n measurements increases the S/N ratio by a factor of $\sqrt{n}$ compared with the value for one measurement. (5%)

(3) The resolution of a chromatographic column is a quantitative measure of its ability to separate analytes A and B. On the basis of the terms given in the opposite Figure,
  (a) define the resolution of a column. (4%)
  (b) if substance A and B have retention times of 16.32 and 17.58 min, respectively, on a 30.0-cm column. The peak widths (at base for A and B are 1.08 and 1.23 min, respectively. Calculate (i) the column resolution and (ii) the length of column required to achieve a resolution of 1.7. (6%)



(4) In every instrument, some stray light (wavelengths outside the bandwidth expected form the monochromator) reaches the detector. Error from stray light is most serious when the absorbance is high because the stray light constitutes a large fraction of the light reaching the detector. If the true absorbance of a sample is 2.00 and there is 1.0% stray light, find the apparent absorbance. (5%)

(5) Explain the difference between (a) SEM and TEM, (b) SAXS and WAXS, (c) AES and ESCA, (d) ISS and SIMS, and (e) DSC and DTA. (10%)

(6) What are the sources of band broadening in ^{13}C spectra of solid? How are lines narrowed so that high-resolution spectra can be obtained? (5%)