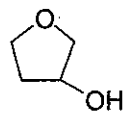
Organic Chemistry

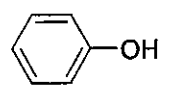
(I) Draw the structures of the following compounds. (8%)

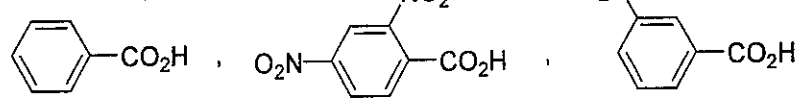
(a) meso-3,4-hexanediol (b) (E)-1-bromo-1-chloropropene (c) thiophene (d) aniline

(II) Rank the following isomers in order of increasing boiling point. (3%)

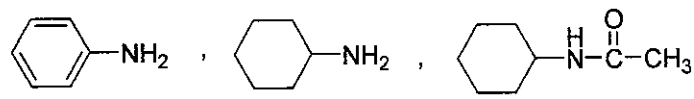
(a)  (b) $CH_3CO_2CH_2CH_3$ (c) $CH_3CH_2CH_2CO_2H$

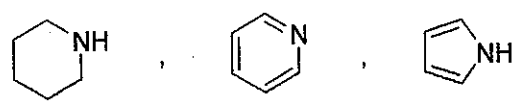
(III) Arrange each group of compounds in order of increasing acidity. (6%)

(a)  , CH_3CH_2OH , CH_3CO_2H

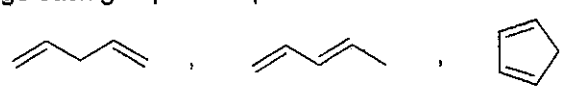
(b) 

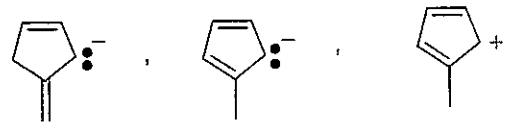
(IV) Arrange each group of compounds in order of increasing basicity. (6%)

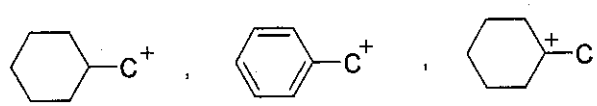
(a) 

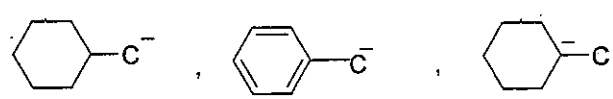
(b) 

(V) Arrange each group of compounds and ions in order of increasing stability (12%)

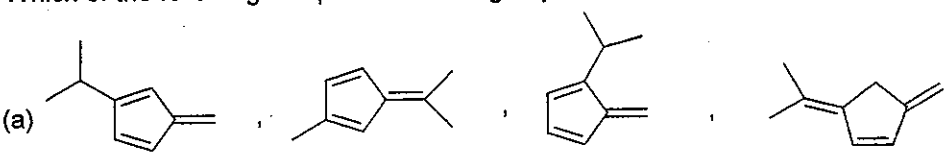
(a) 

(b) 

(c) 

(d) 

(VI) Which of the following compound in each group is more acidic than the others. (6%)

(a) 

(b) $CH_3CH_2CO_2C(O)CH_2CH_3$, $CH_3CH_2C(O)CH_2CO_2CH_3$,

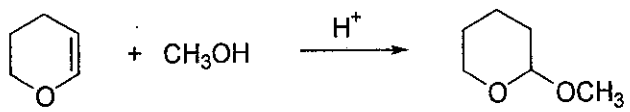
$CH_3C(O)CH_2CH_2CO_2CH_3$

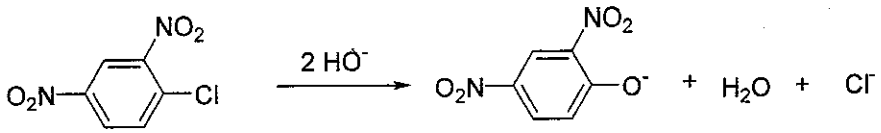
(VII) Give the approximate chemical shift and multiciplicity of the following pairs of compounds in their ^1H NMR spectra. (6%)

(a) CH_3CH_2CHO and $CH_3C(O)CH_3$

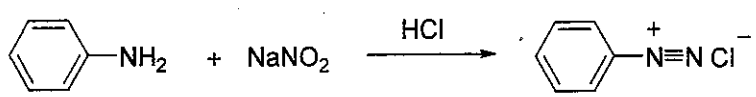
(b) $CH_3CO_2CH_2CH_3$ and $CH_3CH_2CO_2CH_3$

(VIII) Propose mechanisms for the following reactions. (12%)

(a) 

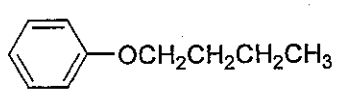
(b) 

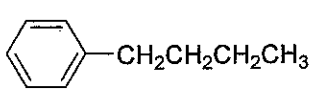
(c) $RCO_2H + SOCl_2 \longrightarrow RC(O)Cl + SO_2 + HCl$

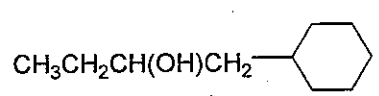
(d) 

(IX) Show how 1-butanol can be converted to the following compounds, using any necessary reagents. (20%)

(a) CH_3CH_2CHO

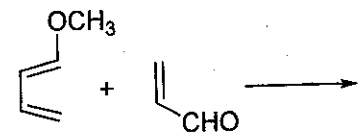
(b) 

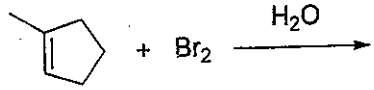
(c) 

(d) 

(e) $CH_3CH_2CH_2CH_2NH_2$

(X) Predict the products of the following reactions. Include stereochemistry where appropriate. (21%)

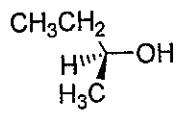
(a) 

(b) 

(c) $CH_3CH(NH_2)CH_2CH_3$ $\xrightarrow[2)\ Ag_2O,\ H_2O\ \ 3)\ heat]{1)\ excess\ CH_3I}$

(d) $CH_3CH_2CO_2CH_3$ $\xrightarrow[excess]{CH_3MgBr}$

(e) $CH_3C(O)CH_2CH_2CO_2CH_3$ $\xrightarrow{NaBH_4}$

(f)  $\xrightarrow[2)NaI/acetone]{1)\ TsCl/pyridine}$

(g) $CH_3CH_2C{\equiv}CCH_3$ $\xrightarrow[quinoline\ (Lindlars\ catalyst)]{H_2/Pd/BaSO_4}$

Inorganic Chemistry

Part I. (30%) Multiple choices: Mark your answers as Y (Yes) or N (No)

(1 point per correct choice, -0.5 point per mistake, 0 point for blank answer.)

For example: Does the following species assume tetrahedral geometry?

(a) $SiMe_4$ (b) $[PtCl_4]^{-2}$ (c) $[AlCl_4]^-$ (d) XeF_4 (e) $Pd(PEt_3)_4$ **Answer: (a) Y (b) N (c) Y (d) N (e) Y**

1. Is the following statement about acid or base CORRECT?
   (a) NH_4^+ is an acid by Arrhenius definition
   (b) NH_3 is a base by Brønsted-Lowry definition
   (c) NH_4^+ and NH_3 are conjugates by Lewis definition
   (d) Higher *Pka* value of an acid means higher acidity for that acid.
   (e) All solutions of salt are of neutral *PH*.

2. Is the following statement about solid-state chemistry CORRECT?
   (a) The packing patterns of LiCl and CsCl in solid are never the same
   (b) Pure ZnS can crystallize in more than one lattice form.
   (c) Hexagonal closest packed structure (hcp) and cubic closest packed (ccp) structures have the same number of tetrahedral holes in their unit cell.
   (d) For M^+X^- metal halide structures whose ionic ratio (r^+/r^-) is higher than 0.414, octahedral coordination is favored for M^+ ion.
   (e) Born-Haber cycle can be used to calculate ionic radii of ionic compounds.

3. Is the following symmetry assignment CORRECT?
   (a) PPh_3 has C_{3h} symmetry
   (b) $[PtCl_4]^{-2}$ has D_{4h} symmetry
   (c) C_{60} has I_h symmetry
   (d) PF_5 has C_{3v} symmetry
   (e) H_2O_2 has *C2* symmetry.

4. Is the following statement about oxygen CORRECT?
   (a) Oxygen molecule at its ground state is diamagnetic.
   (b) Its ground state electronic configuration is $KK\sigma_{2s}^2\sigma^*_{2s}^2\sigma_{2p}^2\pi_{2p}^4\pi^*_{2px}^2$
   (c) It is isoelectronic with NO^+
   (d) Addition of two electrons to it results in peroxide ion.
   (e) It is an oxidant both in air and in solution.

5. Can the following compound be CHIRAL?
   (a) $[Co(NH_2CH_2CH_2NH_2)_3][Cl]_3$
   (b) $Zn[CH_3CH(NH_2)(COO)]_2$
   (c) PdBrClFI
   (d) $CpFe(CO)_2Cl$
   (e) [K(18-crown-6)][NO_3]

(continue on next page)

6. Is the following statement about semiconductor CORRECT?
   (a) Doping As atoms in Si crystal produces p-type semiconductor
   (b) Large band gap makes a good semiconductor
   (c) Chemical Vapor Deposition (CVD) is a common way of making silicon crystals
   (d) Fermi level is the highest orbital at zero temperature
   (e) Doping electron rich material in semiconductor give rise to n-type semiconductivity.

Part II. (70%) Give brief answer to the following questions:

7. (10 points) Draw the δ bonding in $[Re_2Cl_8]^{-2}$ with *d* orbitals that form it.

8. (10 points) The range for ^1H NMR signal of some dinuclear metal complexes are list below. Please explain why they are different.
   Zn(II)/Zn(II) complex: 0-8 ppm; Fe(II)/Fe(II) complex: 0-20 ppm; Fe(II)/Fe(III) complex: 0-200 ppm

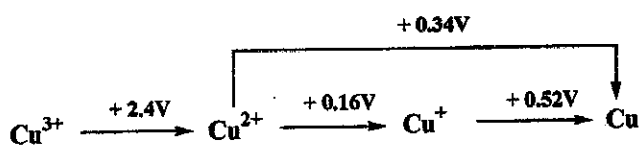
9. (5 points) Why is N_2 extremely stable while P_2 is not? (Hint: For the same reason, C=C double bond is more stable than Si=Si double bond.)

10. (5 points) Please derive and list all possible term symbols (Russell-Saunders terms) for the $2s^22p^2$ configuration of the carbon atom.

11. (10 points) Name two methods and describe what results may be obtained for determining the structure of $CpFe(CO)(PEt_3)I$ (Cp=cyclopentadienyl).

12. (10 points) Describe one possible synthetic method for cis-$PtCl_2(NH_3)_2$.

13. (10 points) In view of the Latimer diagram (standard potentials) given below, explain why Cu^{+2} has higher stability over the other oxidation states.



14. (10 points) Write down the product(s) of the following reactions (indicate NR if no reaction takes place):
   (a) $[Fe(CN)_6]^{3-} + [Co(CN)_6]^{3-}$ →
   (b) $Fe(CO)_5 + h\upsilon$ →
   (c) $Mn_2(CO)_{10} + H_2$ →
   (d) Cp_2Fe (ferrocene) + n-BuLi →
   (e) $B_2H_6 + N(CH_3)_3$ →

--(THE END)--

Physical Chemistry

Chose the right answer (or answers) from the following problems. (4 points for each)

1. Evaluate the ground state energy of a free particle of mass m in a two dimensional box, $0 \le x \le a$, $0 \le y \le 2a$.

   a. $5h^2/8ma^2$ b. $5h^2/32ma^2$

   c. $3h^2/16ma^2$ d. $3h^2/8ma^2$

   e. No answer

2. The harmonic oscillator is a useful model in Quantum Mechanics. Let $\psi_n(x)$ and E_n denote the wave function and energy of a one-dimensional harmonic oscillator, $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$, then, which of the following statement about harmonic oscillator is not true?

   a. $\int \psi_n x \psi_n dx = 0$

   b. $\int \psi_n x^2 \psi_{n+1} dx = 0$

   c. $\left\langle -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \right\rangle = \frac{1}{2}E_n$,

   d. The harmonic oscillator is a perfect model to describe vibration problem of true molecule.

   e. All above are true.

3. If $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$ are quantum mechanical operators of the x, y, z angular momentum components for a moving particle, and $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$, then, which of the following statement is correct?

   a. $\left[\hat{L}^2, \hat{L}_x\right] = -i\hbar\hat{L}_y$

   b. $\hat{L}^2 = -\frac{\hbar^2}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$ in the (r,θ,ϕ) coordinate

   c. All three components can be measured simultaneously.

   d. L_z is the only measurable quantity from experiment.

   e. None of above is correct.

4. Find the normalization constant N of the wave function $\psi(r,\theta,\phi) = Ne^{-r}$, in which

$0 \le r \le \infty$, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$.

(note: $\int_0^\infty x^n e^{-qx} dx = \frac{n!}{q^{n+1}}$, $n > -1$, $q > 0$)

a. $1/\sqrt{2}$ b. $1/\sqrt{\pi}$

c. $1/\sqrt{2\pi}$ d. $1/2$

e. None of above is correct.

5. The fundamental frequency of HCl is 2885 cm^{-1} in the ~~infarad~~ infrared spectra. What would be the fundamental frequency of DCl?

a. 1440 cm^{-1} b. 2040 cm^{-1}

c. 2321 cm^{-1} d. 1886 cm^{-1}

e. None of above is correct.

6. Among the following molecules (H_2, D_2, HD), which has the largest moment of inertia?

a. H_2 b. D_2

c. HD d. They are the same.

e. None of above is correct.

7. In the far infrared spectrum of $H^{79}Br$, there is a series of lines separated by 16.72 cm^{-1}. What is the bond length of the molecule?

a. 1.42 A b. 1.13 A

c. 1.08 A d. 1.24 A

e. None of above is correct.

8. The Hamiltonian of an oscillator is $\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} + x^4$. According to the variation theory, the ground state energy can be calculated by a trial function $\phi(x) = e^{-\alpha x^2/2}$. At what value of α, this trial function gives the best result?

(Note: $\int \phi \frac{d^2}{dx^2}\phi dx = -\frac{\alpha}{2}(\frac{\pi}{\alpha})^{1/2}$, $\int \phi x^4 \phi dx = \frac{3}{4\alpha^2}(\frac{\pi}{\alpha})^{1/2}$, $\int \phi\phi dx = (\frac{\pi}{\alpha})^{1/2}$)

a. 1/4 b. $(6)^{1/3}$

c. $\sqrt{3}$ d. 1/6

e. None of above is correct.

9. Which of the following statement about Zeeman experiment of Hydrogen atom is incorrect?

a. The external magnetic field splits degenerate energy levels.
b. The larger the external magnetic field the better the splitting.
c. The interaction between external magnetic field and electron is proportional to the orbital angular momentum of the electron.
d. The splitting is proportional to the mass of the electron
e. All statements above are correct.

10. The quantum mechanical operators of position and linear momentum are x, y, z and p_x, p_y, p_z respectively. Which of the commutation relation is wrong?

a. Operators x and p_x are not commute.
b. Operators x and p_y are not commute.
c. Operators x and x^2 are always commute.
d. If $[A, B] \neq 0$, then A and B has no common eigenvalue.
e. All answers are correct.

11. The fundamental frequency and rotation constant of CO are 2157 cm^{-1} and 1.925 cm^{-1} respectively. Estimate the transition frequency (in Hertz) from $v=0$, $J=0$ to $v=1$, $J=1$ state. (v, J are vibration and rotation quantum numbers)

a. 6482.55×10^{10}　　b. 6476.78×10^{10}
c. 6465.23×10^{10}　　d. 6459.45×10^{10}
e. None of above is correct.

12. If a container contains 2 moles of ideal gas A, and measured heat capacity C_v of the system is 13.1142 cal · K^{-1}, then what could be C_p value (in cal · K^{-1})?

a. 15.102　　b. 11.1272
c. 17.0882　　d. 9.1402
e. None of above is correct

13. Which of the following property is not a state function?

a. Entropy　　b. Enthalpy
c. Heat　　d. Chemical potential
e. Gibbs Free Energy

14. The Joule-Thomson coefficient of N_2 is assumed to be a constant of value 0.15 K

bar^{-1}. If the N_2 (g) undergoes a drop of pressure of 200 bar, then, the temperature is

a. Raise 30 K
b. Drop 30 K.
c. Keep as constant
d. Drop to its melting point.
e. None of above is correct

15. If an ideal gas is compressed reversibly from 2.25 L at 1.33 bar to 0.8 L, what is the work needed?

a. 410 J
b. 353 J
c. 309 J
d. 275 J
e. None of above is correct.

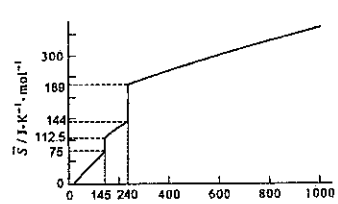
16. Assume ideal behavior, what is the entropy of mixing two moles of N_2 (g) with one mole O_2 (g)?

a. 5.29 J K^{-1}
b. 8.43 J K^{-1}
c. 15.87 J K^{-1}
d. 12.38 J K^{-1}
e. None of above is correct

17. Assuming that heat capacity C_v is independent of temperature for ideal gas A, the entropy change of one mole of A is expanded from 22.4 L at 273 K to 44.8 L at 546 K is ΔS_I; the entropy change of two moles of A are compressed from 44.8 L at 273 K to 89.6 L at 546 K is ΔS_{II}.

a. ΔS_I is negative and ΔS_{II} is positive
b. $2\Delta S_I = \Delta S_{II}$
c. $\Delta S_I = \Delta S_{II}$
d. Molar entropy change $\overline{\Delta S_I} = 1/2\overline{\Delta S_{II}}$
e. None of above is correct.

18. The figure plots standard molar entropy of Cycloproane from 0 K to 1000 K. Base on the figure determines heat of vaporization of the compound.



a. 237.8 J · mol^{-1}
b. 5.44 kJ · mol^{-1}
c. 45 J · mol^{-1}
d. 20.05 kJ · mol^{-1}
e. None of above is correct

19. Which of the following gases has the largest root-mean-square speed at the same temperature: O_2, H_2O, NO_2, N_2.

a. O_2　　b. H_2O

c. NO_2　　d. N_2

e. They all the same

20. A mole of nitrogen is at 1 bar pressure and 298 K. If the temperature is raised to 596 K, then the collision frequency of a single nitrogen molecule in nitrogen is

a. Reduced to half of its original frequency.

b. Doubled its original frequency.

c. Reduced to 0.354 of its original frequency.

d. Increased to 1.414 of its original frequency.

e. None of above is correct.

21. For the thermal decomposition of acetaldehyde

$CH_3CHO \xrightarrow{k_{obs}} CH_4\,(g) + CO\,(g)$

A proposed mechanism is

$CH_3CHO\,(g) \xrightarrow{k_1} CH_3\,(g) + CHO\,(g)$

$CH_3\,(g) + CH_3CHO\,(g) \xrightarrow{k_2} CH_4\,(g) + CH_3CO\,(g)$

$CH_3CO\,(g) \xrightarrow{k_3} CH_3\,(g) + CO\,(g)$

$2\,CH_3\,(g) \xrightarrow{k_4} C_2H_6$

Assuming that the steady-state approximation is valid, then

a. $d[CH_4]/dt = k_2(k_1/k_4)^{1/2}[CH_3CHO]^{3/2}$

b. $d[CH_3]/dt = (k_1/k_2)^{1/2}\,[CH_3CHO]^{1/2}$

c. $d[CH_3CHO]/dt = (k_2/k_3)[CH_3][CH_4]^{1/2}$

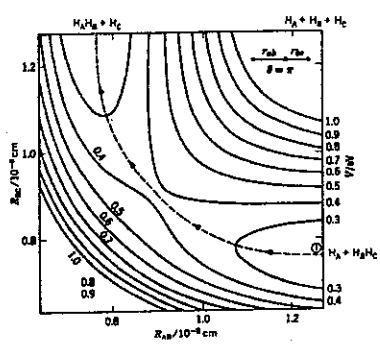
d. $d[CH_3CHO]/dt = k_3[CH_3][CO]$

e. None of above is correct

22. Given in the figure is the potential energy surface for the reaction

$H_A + H_BH_C \longrightarrow H_AH_B + H_C$

The dot line in the figure shows the minimum energy path of the reaction. The three atoms are always in the linear array. Which of the following statement is correct?



a. The energy barrier is less than 0.4 eV

b. The equilibrium bond length of

hydrogen molecule is about 1.3 A

c. The saddle point is around R_{AB} = 1.1 A

d. H_AH_B is more stable than H_BH_C

e. None of above is correct

23. The Maxwell-Boltzmann distribution of molecular velocity in x direction is

$f(v_x) = A\exp(-mv_x^2 / 2k_BT)$

Where m and k_B are the mass of the molecule and Boltzmann constant respectively. Which of the following is the appropriate value of constant A?

(Note: $\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$)

a. $(m/\pi k_BT)^{1/2}$　　b. $(m/2\pi k_BT)^{1/2}$

c. $(m/2\pi k_BT)^{3/2}$　　d. $(m/\pi k_BT)^{3/2}$

e. None of above is correct.

24. The molar entropy $\Delta\bar{S}$ of isothermal expansion of a van der Waals gas.

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

a. $R\ln(\bar{V}_1/\bar{V}_2) - b$　　b. $R\ln\frac{\bar{V}_1-b}{\bar{V}_2-b}$

c. $R\ln(\bar{V}_2/\bar{V}_1)$　　d. $R\ln\frac{\bar{V}_2-b}{\bar{V}_1-b}$

e. None of above is correct.

25. Which of the following conversion is wrong?

a. Femto second = 10^{-15} sec　　b. Pico second = 10^{-12} sec

c. Nano meter = 10^{-8} cm　　d. Micron = 10^{-6} cm

e. All above are correct

國立中山大學九十一學年度碩士班招生考試試題

科目：分析化學(化學系)

1. Calculate the hydroxide ion concentration in a 0.0100 M sodium hypochlorite solution. $K_{a,HOCl} = 3.0 \times 10^{-8}$. (6%)

2. A 50.00-mL aliquot of a solution containing iron(II) and iron(III) required 13.73 mL of 0.01200 M EDTA when titrated at pH 2.0 and 29.62 mL when titrated at pH 6.0. Express the concentration of the solution in terms of the parts per million of each solute. Fe = 55.847 g/mol. (10%)

3. (a) Calculate the thermodynamic potential of the following cell and indicate whether it is galvanic or electrolytic.

$$Pt|UO_2^{2+}(0.0150\ M),\ U^{4+}(0.200\ M),\ H^{+}(0.0300\ M)||Fe^{2+}(0.0100\ M),\ Fe^{3+}(0.0250\ M)|Pt$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\circ = +0.771\ V$$
$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^\circ = +0.334\ V$$

(b) Calculate the equilibrium constant for the reaction

$$U^{4+} + 2H_2O + 2Fe^{3+} \rightleftharpoons UO_2^{2+} + 4H^+ + 2Fe^{2+}$$ (16%)

4. Distinguish between voltammetry, linear scan polarography and pulse polarography. (9%)

5. Describe the basic differences between atomic emission, atomic absorption and atomic fluorescence spectroscopy. For each of these cases, what does one actually measure experimentally? Also, for each of these cases, show quantitatively how the experimental measurements relate to the concentration of the atomic species. (12%)

6. At 580 nm, which is the wavelength of its maximum absorption, the complex $Fe(SCN)^{2+}$ has a molar absorptivity of 7.00×10^3 L cm^{-1} mol^{-1}. Calculate
(a) the absorbance of a 2.50×10^{-5} M solution of the complex at 580 nm in a 1.00-cm cell.
(b) the absorbance of a solution in which the concentration of the complex is twice that in (a).
(c) The transmittance of the solution described in (a).
(d) the absorbance of a solution that has half the transmittance of that described in (a). (10%)

7. Define the following terms of molecular fluorescence spectroscopy:
(a) resonance fluorescence
(b) quantum yield
(c) Stokes shift (10%)

8. Substances A and B have retention times of 16.40 and 17.63 min, respectively, on a 30.0-cm column. An unretained species passes through the column in 1.30 min. The peak widths (at base) for A and B are 1.11 and 1.21 min, respectively. Calculate (a) column resolution, (b) average number of plates in the column, (c) plate height, (d) length of column required to achieve a resolution of 1.5, and (e) time required to elute substance B on the longer column. (15%)

9. A 0.1475 M solution of $Ba(OH)_2$ was used to titrated the acetic acid in a dilute aqueous solution. The following results were obtained.

Sample	Sample volume, mL	$Ba(OH)_2$ volume, mL
1	50.00	43.17
2	49.50	42.68
3	25.00	21.47
4	50.00	43.33

(a) Calculate the concentration of acetic acid in each measurement.
(b) At the 95% confidence level, could any of the results be discarded?
(c) Calculate the mean concentration of acetic acid in this sample.
(d) Calculate the standard deviation for the results.
(e) Calculate the 95% confidence interval for the mean.
Show your calculation. (12%)

Critical Values for the Rejection Quotient Q*

Number of Observations	Q_{crit} 90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

*Reproduced from D. B. Rorabacher, *Anal. Chem.*, **1991**, *63*, 139. By courtesy of the American Chemical Society.

Values of t for Various Levels of Probability

Degrees of Freedom	Factor for Confidence Interval 80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
11	1.36	1.80	2.20	3.11	4.44
12	1.36	1.78	2.18	3.06	4.32
13	1.35	1.77	2.16	3.01	4.22
14	1.34	1.76	2.14	2.98	4.14
∞	1.29	1.64	1.96	2.58	3.29