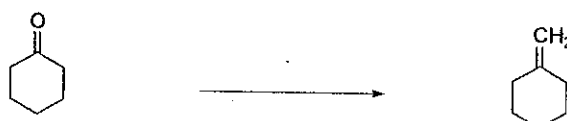請依題序在答案卷上作答，否則不計分。可以不用抄題，但須標明題號。

I. Explain the following terms with text and examples. (20pts)

   (a) Haloform reaction

   (b) Robinson annulation

   (c) Hofmann rearrangement

   (d) Claisen rearrangement

   (e) Stork enamine reaction

II. Use appropriate reagents to complete the following transformations.
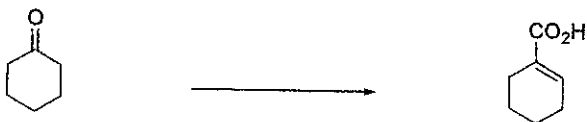   Several reagents may be needed for each transformation. (15 pts)

   (a)

   (b)

   (c)
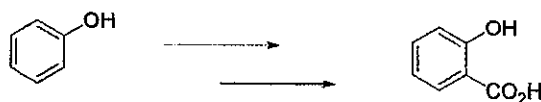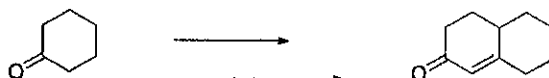

   (d)

   (e)

III. Use the following compounds as starting materials to complete the syntheses.
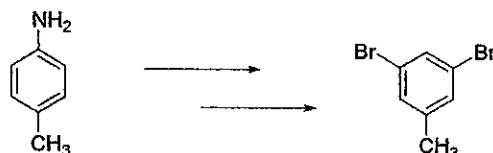Write down each reaction step. (30 pts)

(a)

(b)

(c)

IV. What is the function of quaternary ammonium salt in the reaction below ? (6 pts)

$$\text{CHCl}_3 , \text{NaOH} \qquad R_4\overset{+}{N}\ \overset{-}{Cl}$$
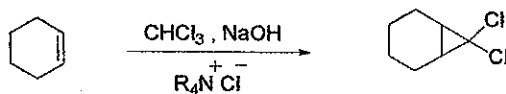
V. Propose mechanisms for the following reactions. (14 pts)

(a)

$$\text{HNO}_2$$
$$\text{H}_2\text{SO}_4$$

(b)

$$\text{excess Br}_2 , \text{NaOH}$$
$$\text{H}^+$$

2
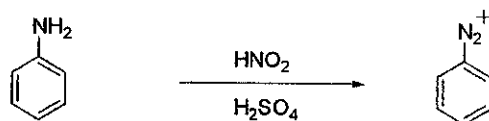
VI. Propose a compound structure based on the given spectral data. (15 pts)
   No points will be counted if no proper interpretation.

114   M^+ ($C_6H_{10}O_2$)

SOLVENT: CCl_4

Impurity
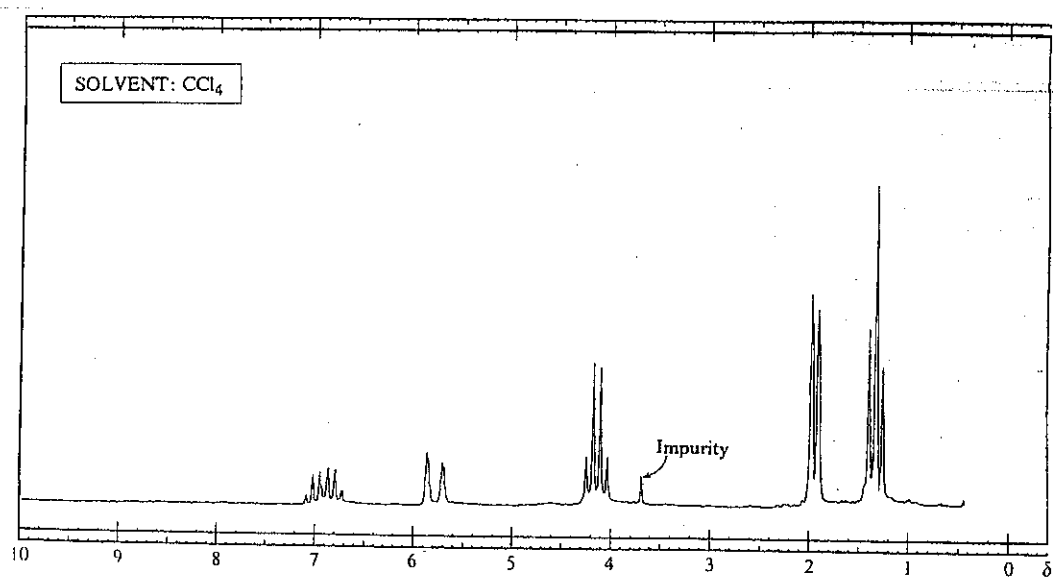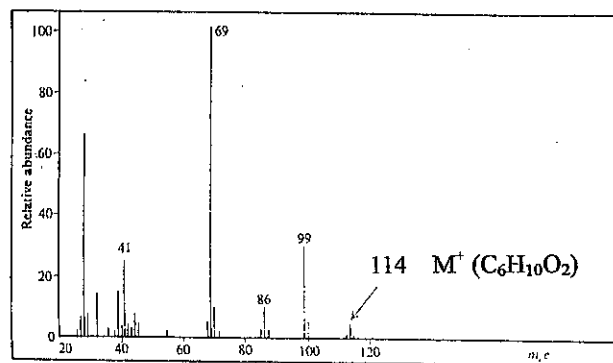
每題 4 分

1) Why is $q_v = \Delta U$ only for a constant volume process? Is this formula valid if work other than P-V work is possible?

2) Under what conditions are ΔH and ΔU for a reaction involving gases identical?
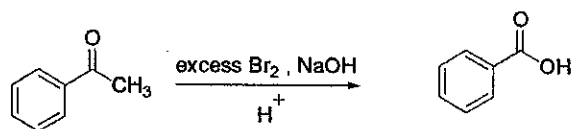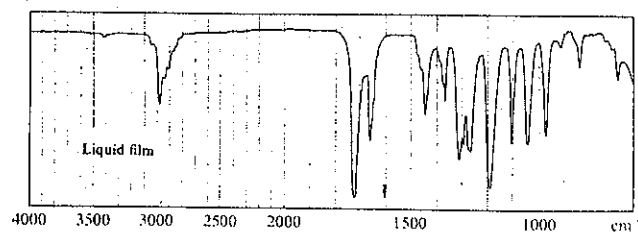
3) You wish to measure the heat of solution of NaCl in water. Would the calorimetric technique of choice be at constant pressure or constant volume? Why?

4) Why is the efficiency of a Carnot heat engine the upper bound to the efficiency of an internal combustion engine?

5) Under what conditions is $\Delta S_{sys} < 0$ for a spontaneous process?

6) Under what conditions is $dA \leq 0$ a condition that defines the spontaneity of a process?

7) Which thermodynamic state function gives a measure of the maximum electric work that can be carried out in a fuel cell? Why?

8) Under what condition is $K_P = K_x$?

9) Why is the magnitude of the boiling point elevation less than that of the freezing point depression?

10) Why are activity coefficients calculated using the Debye–Hückel limiting law always less than one?

11) Why is the zero point energy lower for a He atom in a same sized box than for an electron?

12) Why does the energy of a rotating molecule depend on l, but not on m_l?

13) A molecule in an excited state can decay to the ground state either by stimulated emission or spontaneous emission. Use the Einstein coefficients to predict how the relative probability of these processes changes as the frequency of the transition doubles.

14) Does the initial excitation in Raman spectroscopy take place to a stationary state of the system? Explain your answer.

15) If a spectral peak is broadened, can you always conclude that the excited state has a short lifetime? Why?

16) If the probability density of finding the electron in the $1s$ orbital in the H atom has its maximum value for $r = 0$, does this mean that the proton and electron are located at the same point in space? Why?

17) Write an equation giving the relationship between the Rydberg constant for H and for Li^{2+}.

18) Why are MOs on heteronuclear diatomic molecules not labeled with g and u subscripts?

19) The ground state of O_2^+ is $X^2\Pi_g$ and the next few excited states, in order of increasing energy, are $a^4\Pi_u, A^2\Pi_u, b^4\Sigma_g^-, {}^2\Delta_g, {}^2\Sigma_g^-$, and $c^4\Sigma_u^-$. On the basis of selection rules, which of the excited states can be accessed from the ground state by absorption of UV light?

20) Explain why two magnetic fields, a static field, and a radio-frequency field are needed to carry out NMR experiments.

21) Why do electronic degrees of freedom generally not contribute to the constant volume heat capacity?

22) What is a half-life? Is the half-life for a first-order reaction dependent on concentration?

23) What is the steady-state approximation, and when is this approximation employed?

24) What is a transition state? How is the concept of a transition state used in activated complex theory set?

25) What is the one main assumption in the Lindemann mechanism for unimolecular reactions?

第一到第十題為填充題，每題四分。第十一到第二十二題為簡答題，共六十分。

1. 鈷元素的原子序(Atomic number)是＿＿＿＿＿＿＿＿。

2. 鈷元素的電子組態(Electron configuration)是 ＿＿＿＿＿＿＿＿。

3. 鈷正三價陽離子的電子組態是 ＿＿＿＿＿＿＿＿。

4. 只考慮電子自旋對磁性的貢獻(Spin only)，則預期正八面體具高自旋特性的鈷正三價錯合物的磁矩(Magnetic moment)為 ＿＿＿＿＿＿＿＿ BM。

5. 鈷元素電子基態的能態符號(Term symbol)是 ＿＿＿＿＿＿＿＿。

6. NH_3, Cl^-, 和 $H_2N(CH_2)_2NH_2$ 當配子(Ligand)時，其供電子生成 sigma 鍵結的能力(Sigma donating ability)，依大到小排列為 ＿＿＿＿＿＿＿＿。

7. $[CoCl(NH_3)_5]^{2+}$錯合物結構具有的點群是 ＿＿＿＿＿＿＿＿。

8. 面心立方體中，所含正四面體的孔洞數為 ＿＿＿＿＿＿＿＿。

9. O_2^+的鍵級(Bond order)是 ＿＿＿＿＿＿＿＿。

10. BF_3分子中，硼的形式電荷是＿＿＿＿＿＿＿＿。

11. 寫出下列各反應的正確平衡方程式。(十二分)

    (a) $PCl_5 + H_2O \rightarrow$

    (b) $2\,PCl_5 + 8\,H_2O \rightarrow$

    (c) $Hg + Zn(C_2H_5)_2 \rightarrow$

    (d) $SiO_2 + 6\,HF \rightarrow$

12. 已知下列二反應式為真

$TiCp_2H(CH_3) + ROH \rightarrow TiCp_2(OR)(CH_3) + H_2$

$MnH(CO)_5 + ROH \rightarrow$ no reaction

簡述其理。(四分)

13. 畫出下列各物的路易士結構，並以立體結構圖表示其形狀。(四分)

    (a) XeF_5^+

    (b) $S_2O_3^{2-}$。

14. 畫出$[Co(NH_3)_6]^{3+}$的軌域能階圖(Orbital energy level)。(四分)

15. 指出何者為較強的路易士酸(Lews acid)。並簡述其理。(四分)

    (a) $BeCl_2$ 和 BCl_3

    (b) $B(n\text{-}Butyl)_3$ 和 $B(t\text{-}Butyl)_3$

16. 已知 $Fe^{3+} \xrightarrow{\ 0.77V\ } Fe^{2+} \xrightarrow{\ -0.44V\ } Fe$

    則 Fe^{2+} 是否會產生自發性不均(Disproportionation)反應？簡述其理。(四分)

17. 下列何者可能為強氧化劑？簡述理由。(四分)

    $[Fe(CO)_4]^{2-}$, $[Fe(\eta^5\text{-}C_5H_5)_2]^+$, $LiAlH_4$

18. 簡單的鐵 porphyrin 錯合物，何以不似血紅素般，可用作氧氣的載子(Carrier)？

    (四分)

19. 以紫外光照射二氧化鈦，可增加其導電性。簡述其理。(四分)

20. 若以線性分子的核間軸定為 Z 方向，畫出 HF 分子中，以氫原子的 1s 軌域和 F 原子的 $2p_z$ 軌域組成的結鍵軌域(bonding orbital)和反結鍵軌域(antibonding orbital)的分子軌域定性輪廓圖；並畫出其可能的 HOMO 軌域輪廓圖。(六分)

21. 畫出 $[CoCl(NH_3)_5]^{2+}$ 錯合物的軌域能階圖。(五分)

22. 下列物質，進行水取代反應，請依其反應速率由快到慢排列。(五分)

    $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$, $[Mn(OH_2)_6]^{2+}$, $[Ni(OH_2)_6]^{2+}$

1. (a) What is the difference between qualitative and quantitative analysis? (4%)

   (b) Explain the difference between systematic and random errors. (8%, 12% total)

2. Describe the preparation of 100 mL of 1.00 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37 wt% HCl (36.5 g/mol). (8%)

3. (a) Find the pH of a solution prepared by dissolving 12.43 g of Tris [$(HOCH_2)_3CNH_2$, 121.135 g/mol] plus 4.67 g of Tris hydrochloride [$(HOCH_2)_3CNH_3^+Cl^-$, 157.596 g/mol] in 1.00 L of water $pK_{Tris \cdot HCl} = 8.072$ (6%)

   (b) If we add 12.0 mL of 1.00 M HCl to the solution in (a), what will be the new pH. (4%, 10% total)

4. (a) Calculate the thermodynamic potential of the following cell and indicate whether it is galvanic or electrolytic. (10%)

   Pt | U^{4+} (0.200 M), UO_2^{2+} (0.0150 M), H^+ (0.0300 M) ‖

   Fe^{2+} (0.0100 M), Fe^{3+} (0.0250 M) | Pt

   $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^0 = 0.771$ V

   $UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$ $E^0 = 0.334$ V

   (b) Calculate the equilibrium constant for the reaction

   $U^{4+} + 2H_2O + 2Fe^{3+} \rightleftharpoons UO_2^{2+} + 4H^+ + 2Fe^{2+}$ (5%, 15% total)

5. Describe the basic operating principles of atomic emission, atomic absorption and atomic fluorescence spectroscopy. For each of these methods, what does one actually measure experimentally? Also, for each of these methods, show quantitatively how the experimental measurements relate to the concentration of the atomic species. (15%)

6. A 50.0-mL aliquot of well water is treated with an excess of KSCN and diluted to 100.0 mL. Calculate the parts per million of iron(III) (55.9 g/mol) in the sample if the diluted solution has an absorbance of 0.506 at 580 nm when measured in a 1.50-cm cell. The molar absorptivity of $FeSCN^{2+}$ is 7.00 x 10^3 L/cm · mol at 580 nm. (8%)

7. (a) How do gaseous and desorption ionization sources for mass spectrometry differ? (6%)

   (b) Describe the causes of the energy distribution of ions leaving ionization source. Why do double-focusing mass spectrometers give narrow peaks and higher resolution? (6%, 12% total)

8. Define (a) selectivity factor (b) longitudinal diffusion (c) plate height (d) gradient elution in liquid chromatography (e) electroosmotic flow. (20%)