國立清華大學 102 學年度碩士班考試入學試題

系所班組別：生醫工程與環境科學系 乙組（環境分子科學組）
考試科目：(2301)普通化學　　共__8__頁，第__1__頁　　*請在【答案卷、卡】作答

(I) Multiple Choices. Please choose the one alternative that best answers the question. (44%, 2% of each)
請在答案卡作答區內作答

1. The successive ionization energies of a certain element are I_1 = 577.9 kJ/mol, I_2 = 1820 kJ/mol, I_3= 2750 kJ/mol, I_4 = 11,600 kJ/mol, and I_5 = 14,800 kJ/mol. This pattern of ionization energies suggests that the unknown element is:

(A) K　(B) Al　(C) Cl　(D) Se　(E) Kr

2. It is determined that the charcoal in a fire pit used as an ancient hearth has lost about 42.3% of the initial ^{14}C. How old was the fire pit if ^{14}C has a half life of 5730 years?

(A) 2210 yrs　(B) 4430 yrs　(C) 4550 yrs　(D) 5250 yrs　(E) 7750 yrs

3. An important reagent in organic chemistry is thionyl chloride, $SOCl_2$. One synthetic route would be to react SO_2 with HCl in the gas phase to produce $SOCl_2$ and water. What is the entropy change for this reaction (J/mol·K $SOCl_2$) if the coefficient of $SOCl_2$ in the balanced equation of reaction is 1? (S° = 309.7 ($SOCl_2$), 248.2 (SO_2), 186.9 (HCl), 188.8 (H_2O) in J/mol·K)

(A) –123　(B) 123　(C) –246　(D) –146　(E) 61.5

4. The complexes $Co(NH_3)_6^{3+}$ and $Mo(CO)_6$ are isoelectronic and diamagnetic. The first complex is orange and the second complex is white. What can you deduce about the value of Δ in both of these complexes?

(A) Δ is larger in $Mo(CO)_6$ than in $Co(NH_3)_6^{3+}$　(B) Δ is 0 in $Mo(CO)_6$
(C) Δ is smaller in $Mo(CO)_6$ than in $Co(NH_3)_6^{3+}$　(D) Δ is the same in the two complexes
(E) none of the above

5. Sea water has about 0.46 mol of NaCl and 0.065 mol of $MgCl_2$ in every liter. What is the vapor pressure of sea water at 30°C if pure water would have a vapor pressure of 33.2 mm Hg? (assume there are 1000 grams of water in 1 L of sea water)

(A) 33.2 mm Hg　(B) 32.5 mm Hg　(C) 37.0 mm Hg
(D) 30.3 mm Hg　(E) 32.9 mm Hg

6. A solution of total volume 0.50 L was prepared by the addition of 0.10 mol of KF to sufficient water. From the following, select the major species and the pH of the solution. The K_a value for HF is 7.2×10^{-4}.

(A) K^+. HF; HO^-, H_2O, pH = 8.23　(B) K^+. F^-; H^+, H_2O, pH = 5.76
(C) K^+, H_2O, F^-, pH = 8.23　(D) K^+, H_2O, F^-, pH = 5.76
(E) None of the above

7. The reaction of NO with O_2 to give oxygen is known to follow a third order rate law (rate = $k[NO]^2[O_2]$). Two possible mechanisms are shown below.

<u>Mechanism 1</u>

$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$ (slow)

<u>Mechanism 2</u>

$2\ NO\ (g) \rightleftharpoons (NO)_2\ (g)$ (fast)

$(NO)_2 + O_2 \rightarrow 2\ NO_2$ (slow)

Which of these two mechanisms is a more acceptable mechanism, based on the criteria given above?

(A) Mechanism 1 because it is simpler

(B) Mechanism 1 because its rate law is the same as the known rate law

(C) Mechanism 2 because it only involves 2 steps

(D) Mechanism 2 because only bimolecular processes are involved

(E) Mechanism 1 because no unstable species are formed

8. Consider the H atoms in **bold** print in the following compounds.

A= $CH_3C\mathbf{H}_2(C{=}O)CH_3$　　B = $C\mathbf{H}_3CH_2(C{=}O)CH_3$　　C= $C\mathbf{H}_3CH_2CH_2(C{=}O)CH_3$

D= $CH_3CH_2(C{=}O)C\mathbf{H}_2(C{=}O)CH_3$

Select the sequence where the bold H atoms are in order of increasing acidity.

(A) D, B, A　　(B) A, B, D

(C) C, B, A　　(D) A, C, D

(E) D, A, C

9. Consider a warm (30°C) 355 mL can of soda, under 2.5 atm CO_2 pressure. What volume of CO_2 will be released from the soda in order to reach equilibrium after opening to the room where the pressure of $CO_2 = 3.25\times10^{-4}$ atm and the total pressure is 758 mm Hg ($K_H = 1.6\times10^{-2}$ M/atm)?

(A) 3.5 mL　　(B) 3.5 L　　(C) 35 mL　　(D) 0.35 L　　(E) 100 mL

10. Which of the following selections has the molecules arranged in order of increasing standard entropy? (one mol of each substance is being compared)

(A) C(*graphite*), $C_{60}(s)$, C(*diamond*)

(B) $Si(s)$, $P_4(s)$, $S_8(s)$

(C) $C_2H_6(g)$, $C_2H_4(g)$, $CH_4(g)$

(D) Polystyrene (made of 1000 monomer units), DNA (1000 base pairs), polyethylene (1000 monomer units)

(E) None of the above

11. The following reaction takes place at 80.1°C.

$$Ru(NH_3)_5Cl^{2+}\ (aq) + H_2O\ (l) \rightarrow Ru(NH_3)_5(H_2O)^{3+}\ (aq) + Cl^-\ (aq)$$

The following time and concentration data are collected.

t (s)	$[Ru(NH_3)_5Cl^{2+}]$ (M)	$\ln [Ru(NH_3)_5Cl^{2+}]$	$1/[Ru(NH_3)_5Cl^{2+}]$
0	1.50×10^{-2}	-4.20	66.7
1.00×10^{-3}	1.08×10^{-2}	-4.53	92.6
2.00×10^{-3}	7.78×10^{-3}	-4.86	128.5
3.00×10^{-3}	5.61×10^{-3}	-5.18	178.2
5.40×10^{-3}	2.55×10^{-3}	-5.97	392
1.01×10^{-2}	5.46×10^{-4}	-7.51	1830
4.00×10^{-2}	3.01×10^{-8}	-17.3	3.32×10^{7}

Which of the following is the correct value of the rate constant?

(A) 3.28 1/M·s　(B) 4.19 1/s　(C) 419 1/s　(D) 328 1/M·s　(E) 328 1/s

12. Which of the following does not have delocalized π bonding?

(A) NO_2　(B) SO_2　(C) F_2O　(D) NO_2^+　(E) O_3

13. Which of the following provides the greatest energy?

(A) 5.00×10^{10} photons of frequency 1.00×10^{9} s^{-1}

(B) 7.00×10^{6} photons of wavelength 550 nm

(C) 5.00×10^{5} photons of frequency 1.05×10^{14} s^{-1}

(D) 7.20×10^{8} photons of wavelength 200 nm

(E) 5.00×10^{15} photons of wavelength 15 m

14. CO_2 can be liquefied under high pressure and moderate temperatures. Which of the following substances would be expected to dissolve in liquid CO_2?

(A) $CH_3CH_2CH_2CH_3$　(B) SF_6　(C) CH_3COCH_3

(D) Benzene, C_6H_6　(E) All of the above

15. A glass bulb with a volume of 250.0 mL contains a small amount of solid potassium chlorate. It is connected to a mercury manometer. Upon heating the bulb, the following (unbalanced) reaction occurs:

$$KClO_3 \rightarrow KCl + O_2$$

After the apparatus cools back to room temperature, 23°C, the difference in the mercury levels in the manometer is now 14.2 cm. Which of the following statements are true?

1. The mercury on the side of the tube connected to the manometer is higher than before.
2. About 1.9×10^{-3} mol $KClO_3$ decomposed
3. About 0.16 g $KClO_3$ decomposed
4. The mercury on the side of the tube connected to the manometer is lower than before.
5. About 1.3×10^{-3} mol O_2 were evolved

(A) 1, 2 and 5 only　(B) 5 only　(C) 2 and 4 only
(D) 3 and 4 only　(E) 4 and 5 only

16. The activation energy of a certain uncatalyzed reaction is 64 kJ/mol. In the presence of a catalyst, the activation energy E_a is 55 kJ/mol. How many times faster is the catalyzed than the uncatalyzed reaction at 400°C? Assume that the frequency factor remains the same.

(A) 5.0 times　(B) 1.16 times　(C) 15 times
(D) 2.0 times　(E) 0.2 times

17. For the reaction given, which half reaction occurs at the anode?

$$2\ H_2\,(g) + O_2\,(g) \rightarrow 2\ H_2O\ (l)$$

(A) $H_2 \rightarrow H_2O$
(B) $O_2 \rightarrow H_2O$
(C) $H_2O \rightarrow H_2$
(D) $H_2O \rightarrow O_2$
(E) None of the above

18. The reactions of Group 13 chlorides (BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$) with bases are predicted well by the HSAB principle. Which of the following is the predicted order of reactivity (completeness of adduct formation) of these compounds toward $P(CH_2CH_3)_3$?

(A) $AlCl_3 < InCl_3 < BCl_3 < GaCl_3$
(B) $BCl_3 < GaCl_3 < AlCl_3 < InCl_3$
(C) $BCl_3 < AlCl_3 < GaCl_3 < InCl_3$
(D) $AlCl_3 < BCl_3 < GaCl_3 < InCl_3$
(E) $InCl_3 < GaCl_3 < AlCl_3 < BCl_3$

19. A solution is made by the addition of 0.34 mol of Na_2HPO_4 and 0.65 mol of NaH_2PO_4 and sufficient water to give a total volume of 1.2 L. How many grams of NaOH would need to be added to increase the pH by 0.2 pH units?
(A) 0.34　(B) 3.4　(C) 4.4　(D) 5.4　(E) 6.5

20. The primary reason that an ionic compound of formula KCl_2 does not form is:
(A) The lattice energy is smaller than that of KCl
(B) The electron affinity of Cl is endothermic
(C) The bond energy of Cl_2 is prohibitively large
(D) The total ionization energy to reach K^{2+} is too high
(E) all of the above

21. An electron in an H atom is excited to an energy of -2.42×10^{-19} J. What is the largest value of m_l possible for this energy level?
(A) 1　(B) 2　(C) 3　(D) 0　(E) none of the above

22. Dimethyl hydrazine, $(CH_3)_2N–NH_2$, is a liquid at room temperature. How many atoms in this molecule have trigonal pyramidal geometry?
(A) 1　(B) 2　(C) 3　(D) 4　(E) 5

(II) Short Answer Questions (56%)　<u>請在答案卷作答區內作答</u>

1. (6%) Consider three identical flasks filled with different gases.
Flask A: CO at 760 torr and 0°C
Flask B: N_2 at 250 torr and 0°C
Flask C: H_2 at 100 torr and 0°C
(a) In which flask will the molecules have the greatest average kinetic energy?
(b) In which flask will the molecules have the greatest root mean square velocity?
(c) Which flask will have the greatest number of collisions per second with the walls of the container?

2. (3%) For the species O_2, O_2^+, and O_2^-, give the electron configuration and the bond order for each. Which has the strongest bond?

3. (3%) How would you make a buffer of pH = 3.75 from the following solutions with a total volume of 450 ml? ($K_a = 1.77\times10^{-4}$ for Formic Acid, HCO_2H)
0.100M NaHCOO　0.100 M $HClO_4$　0.100 M NaOH　0.100 M NH_3

4. (6%) Consider the galvanic cell based on the following half-reaction:

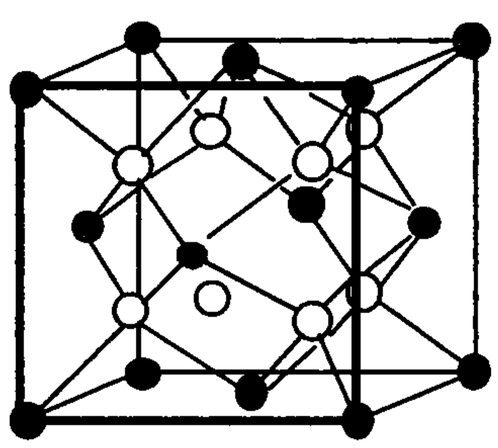
$$Au^{3+} + 3e^- \rightarrow Au \qquad E° = 1.50\ V$$
$$Tl^{+} + e^- \rightarrow Tl \qquad E° = -0.34\ V$$

(a) Determine the overall cell reaction and calculate $E°_{cell}$

(b) Calculate $\Delta G°$ and K for the cell reaction at 25°C.

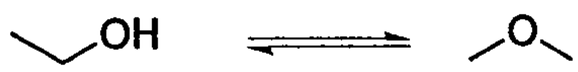
(c) Calculate $E°_{cell}$ at 25°C when $[Au^{3+}] = 1.0\times10^{-2}$ M and $[Tl^{+}] = 1.0\times10^{-4}$ M.

5. (3%) The figure shows the unit cell of a compound containing A (open spheres) and X (shaded spheres). What is the empirical formula of this compound if the shaded spheres form a face centered cubic arrangement and the open spheres are contained within the unit cell?



6. (4%) Ben Franklin determined Avogadro's number within a factor of 5. He was able to do this by dropping 1 teaspoon of oil on a still pond and determined the area covered by the oil at about ¾ of an acre. You can simulate this by adding 1 drop of soap on the top of a greasy pan in the kitchen and watch the grease move to the sides. Sketch the interaction of the soap with the layer of water and sketch how the soap "dissolves" grease in water.

7. (5%) The possible isomerization for ethanol to methyl ether at 25°C and 1 atm is shown below:



	Ethanol (*g*)	Methyl ether (*g*)
$\Delta H_f°$ (kJ/mol)	-235.4	-184.05
$S°$(J/mol·K)	282	267.1

What is (a) the value of the reaction quotient when $\Delta G = 0$ and (b) will the predominant species be ethanol or methyl ether?

8. (2%) In the following set, which atom or ion has the smallest radius?
S, Cl, Kr

9. (2%) Draw the ground state energy level diagram for Cu^{2+}.

10. (5%) When 2.0 mol of SO_2 (g) react completely with 1.0 mol of O_2 (g) to form 2.0 mol of SO_3 (g) at 25°C and a constant pressure of 1.0 atm, 198 kJ of energy are released as heat. Calculate ΔH and ΔE for this process.

11. (3%) Draw the 2 structural isomers of $C_2H_3Cl_3$ and determine which isomer has the greater dipole moment.

12. (4%) The partial pressure of an equilibrium mixture of N_2O_4 (g) and NO_2 (g) are $P_{N_2O_4} = 0.34$ atm and $P_{NO_2} = 1.20$ atm at a certain temperature. The volume of the container is doubled. Find the partial pressures of the two gases when a new equilibrium is established.

13. (6%) The K_{sp} for HgS is 1.6×10^{-54} and the overall formation constant for $Hg(CN)_4^{2-}$ is 4.0×10^{41}.
(a) Please calculate the equilibrium constant for the reaction.

$$HgS\,(s) + 4CN^-(aq) \rightleftharpoons Hg(CN)_4^{2-}(aq) + S^{2-}(aq)$$

(b) What is the value of the reaction quotient Q_{sp} when 1.1 mg of HgS is added to 1.0 L of 0.01 M NaCN and will all of the HgS dissolve?

14. (4%) Draw the Lewis structure of O_2F_2. Assign oxidation states and formal charges to the atoms in O_2F_2. The compound O_2F_2 is a vigorous and potent oxidizing and fluorinating agent. Are oxidation states or formal charges more useful in accounting for the properties of O_2F_2?

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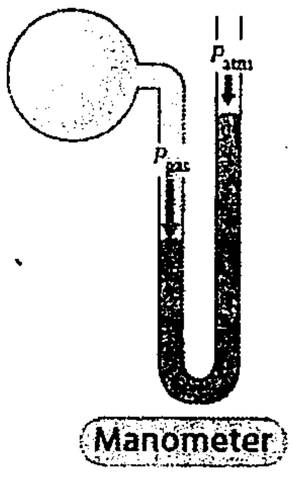
1. $E_n = \frac{-2.178\times10^{-18}\text{J}}{n^2}$

2. $c = 3.0\times1^{08}$ m/s, $h = 6.626\times1^{0\text{-}34}$ J·s

3. $R = 0.082$ L·atm/mol·K

4. $R = 8.314$ J/mol·K

5. 

6. Periodic table

1 H 1.008																	2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
87 Fr [223.02]	88 Ra [226.03]	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 Fl [289.19]	115 Uup [288.19]	116 Lv [293]	117 Uus [294]	118 Uuo [294]

anthanoids *	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05
*Actinoids **	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]