Chemistry II Final Exam

18:00-21:00, 17 June, 2016 (Total Score: 119 points)

1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.008	2 2A																2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 *La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 †Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (268)	110 Ds (271)	111 Rg (280)	112 Uub		114 Uuq		116 Uuh		118 Uuo

*Lanthanide series	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
†Actinide series	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Constants

R = 8.314 J/mol·K = 0.08205 L·atm/mol·K = 8.314 L·kPa/mol·K = 0.08314 L·bar/mol·K

1. What are the units of the rate constant for a reaction of order n? (5%)

2. Answer the following short questions: (2% for each, 24% total)
   (a) How is it possible that the order of some reactions is fractional?
   (b) What is a pseudo-first-order reaction?
   (c) Write down the rates of changes of A, B, and C for the following parallel elementary reactions

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

   (d) Write down the rates of changes of A, B, and C for the following consecutive elementary reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

   (e) Write down the rates of changes of A and B for the following reversible elementary reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

(f) What is the relationship between the equilibrium constant K and the rate constants k_1 and k_{-1} for the following reversible elementary reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

(g) Write down the Arrhenius equation.

(h) Which of the two reaction steps is the rate-determining step for the following consecutive reactions?

$$A \xrightarrow{k} B \xrightarrow{10k} C$$

(i) How is a catalyst able to increase the reaction rate?

(j) What is heterogeneous catalysis?

(k) What is the rate of production of the product P in the enzymatic reaction

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES$$
$$ES \xrightarrow{k_2} E + P$$

according to the model introduced by Michaelis and Menten?

(l) What is the definition of the Michaelis constant K_M?

3. What is the half-life time of a compound if 80% of a given sample of the compound decomposes in 60 min? Assume first-order kinetics. (6%)

4. The rate for the reaction $2\ NO_2(g) \rightarrow N_2O_4(g)$ is given by rate = $k[NO_2]^2$. Will the following changes affect the value of k? (2% for each, wrong answer is -1% 答錯倒扣 1%)
   (a) The pressure of NO_2 is doubled.
   (b) Isotope substitution of nitrogen in NO_2 from ^{14}N to ^{15}N.
   (c) The volume of the container is doubled.
   (d) The temperature is decreased by 10°C.
   (e) A catalyst is added to the container.

5. Answer the following questions related to manganese. (34% total)
   (a) What is the electron configuration of a manganese atom? (2%)
   (b) What is the electron configuration of a gas phase manganese ion in the +2 oxidation state? (2%)
   (c) What is the formula of the complex formed when the manganese ion mentioned in (b). dissolves in water? (2%)

(d) Would heptawatermanganese(II) be a correct name for this complex? If not, what should be the name? (4%)
(e) What is the structure of the complex? (2%)
(f) Discuss whether the d orbitals in the metal of the complex have the same energy? (6%)
(g) The complex is a high-spin complex. Explain the meaning of "high-spin complex". (6%)
(h) Write down the number of electrons in each one the d orbitals in the metal of the complex. (2%)
(i) How many parallel spins do you expect? (2%)
(j) Is the complex diamagnetic or paramagnetic? (2%)
(k) When two ligands of the complex are replaced by another type of ligand L, how many isomers may exist for the new complex? (2%)
(l) According to the spectrochemical series, arrange the following ligands in increasing order of their abilities to split the d-orbital energy levels.
ammonia, bromide, carbon monoxide. (2%)

6. A compound X contains only C, H, and O. The combustion of 150.0 mg of X with excess oxygen gave 356.8 mg of CO_2 and 182.4 mg of H_2O. (a) Derive the empirical formula of X. (b) Via the boiling-point elevation test, the molar mass of X is found in the region of 50~120 g/mol. And it's also found that X does not react with sodium metal and can not disolve in water. Draw the line structure for X. If there were more than one possible structures, draw all of them. (3+3%)

7. Are the following systematic names correct or not? (1% for each, 6% total)
(a) 1-pentanone
(b) 2,2-dichloro-3-methylhexane
(c) 2-propyne
(d) 3-diethyloctane
(e) ethanamine
(f) butanoic acid

8. Are of the following statements about RNA correct or not? (1% for each, 5% total)
(a) Each of the repeating units in RNA contains one phosophate.
(b) Each of the repeating units in RNA contains one deoxyribose.
(c) Four bases: A, T, C, and G are found in both DNA and RNA.
(d) Typically, a RNA molecule does not exist as a double-helical strand as a DNA molecule.
(e) Typically, a RNA moldcule has a larger molar mass than a DNA molecule.

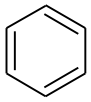
9. (a) What is a “condensation reaction”? (b) Please give an example. (2+2%)

10. When the peptide Y containing nine amino acid resides was hydrolyzed, it gave the following smaller fragments: Gly-Ala-Phe , Ala-Leu-Val , Gly-Ala-Leu , Phe-Glu-His ,and His-Gly-Ala. Please reconstruct the amino acid sequence in this peptide Y. (3%)

11. Fill the correct answers. (2% for each answer, total 16%)

(a) n _____ → $-(-CH_2-CH=CH-CH_2-)-_n$

(b)



+ Br_2 $\xrightarrow[\text{catalyst}]{FeBr_3}$ _____ + _____

It is a _____ reaction. (A) elimination, (B) addition, (C) substitution, (D) radical

(c) $CH_3CH_2OH + Na \rightarrow$ _____ + _____

(d) $C_7H_{15}COOCH_3$ (methyl octanoate) + H_2O $\xrightarrow[\text{catalyst}]{NaOH}$ _____ + _____

104B Chemistry (II) Final Exam

Answer

1. **5%**

The rate of a reaction of order n is defined by the following equation

$$\frac{d[A]}{dt} = k\,[A]^n$$

The units of the left-hand-side are M/s, the units of the right-hand-side are the units of k multiplied by M^n. Equality of both sides gives for the units of k

units of $k = M^{1-n} \cdot s^{-1}$

2. **每題 2%，共 24%**

(a) The order of elementary reactions is never fractional. But sometimes a given chemical reaction, being a complicated sequence of elementary reactions with integer-like order, appears as a single elementary reaction with fractional order due to complicated form of solutions to the coupled differential equations describing the complicated sequence of elementary reactions. (Example 14.10, p.749)

(b) This is a higher-order reaction, which behaves as a first-order reaction in A, because the concentration of all other reagents is so high that it practically does not change during the reaction. The rate of such a reaction is linear in $[A]$. (p.733)

(c) (p.734) **每寫對一個算式得 1%，最多得 2%**

$$\frac{d[A]}{dt} = -(k_1 + k_2)\,[A]$$

$$\frac{d[B]}{dt} = k_1\,[A]$$

$$\frac{d[C]}{dt} = k_2\,[A]$$

(d) (p.734) **每寫對一個算式得 1%，最多得 2%**

$$\frac{d[A]}{dt} = -k_1\,[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2\,[B]$$

(e) (p.734) **每個算式 1%**

$$\frac{d[A]}{dt} = -k_1\,[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

(f) (p.734) $K = k_1 / k_{-1}$

(g) (p.736) $k = A \cdot \exp\left(-\frac{E_A}{RT}\right)$

(h) (p.735) The first step $A \xrightarrow{k} B$

(i) (p.754) Catalysts are able to modify the sequence of elementary reactions in such a way that the highest point on the potential energy path between the substrates and products in the presence of a catalyst is located much lower than the highest point on an analogous map in the absence of a catalyst. We usually describe this phenomenon as "lowering of the activation energy".

(j) (p.755) Catalysis process in which the reagents and the catalyst are in different phases.

(k) (p.762) rate $= \frac{k_2[E]_0[S]}{K_M+[S]}$

(l) (p.762) $K_M = \frac{k_{-1}+k_2}{k_1}$

3. **6%**

For a first-order kinetics, we have $\frac{d[A]}{dt} = -k\,[A]$

which gives after integration $\ln\frac{[A]}{[A]_0} = -kt$ or alternatively $[A] = [A]_0 \exp(-kt)$

Substituting the data given in the problem ($[A] = \frac{[A]_0}{5}$ and $t = 3600$ s), we can compute k

$k = -\frac{1}{t}\ln\frac{[A]}{[A]_0} = -\frac{\ln\frac{1}{5}}{3600}\,s^{-1} = \frac{\ln 5}{3600}\,\mathrm{s}^{-1}$ **(分段給分：3%)**

Using this value of k computed above, we can proceed to the computation of the half-life time $\tau_{1/2}$. Since $t = -\frac{1}{k}\ln\frac{[A]}{[A]_0}$

we have $\tau_{1/2} = -\frac{1}{k}\ln\frac{\frac{1}{2}[A]_0}{[A]_0} = \frac{3600}{\ln\frac{1}{5}}\ln\frac{1}{2}\ \mathrm{s} = \frac{\ln 2}{\ln 5}\cdot 3600\ \mathrm{s} \cong 1550.4\ \mathrm{s} \cong 25.8\ \mathrm{min}$

(分段給分：3%)

4. **每題 2%，答錯倒扣 1 分，共 10%。不需要寫理由**

(a) No

(b) Yes

Since the reaction proceeds in the gas phase, the frequency factor A in Arrhenius equation can be estimated using the collision theory. According to the derivations given on p.741 of Laird, the frequency factor A is proportional to $m^{-1/2}$, where m is the mass of the reacting molecule. Isotope substitution of nitrogen will modify m, and consequently will alter A and k.

(c) No

(d) Yes

The rate constant *k* is temperature dependent.

(e) Yes

Adding a catalyst alters the reaction pathway and leads to a smaller activation barrier, which via the Arrhenius equation increases the rate constant *k*.

5. **共 34%**

(a) $[Ar]4s^2 3d^5$ **(2%)**

(b) $[Ar]3d^5$ **(2%)**

(c) $[Mn(H_2O)_6]^{2+}$ **(2%)**

(d) No **(2%)**

hexaaquomangaese(II) ion or hexaaquamangaese(II) ion **(2%)**

(e) Octahedral **(2%)**

(f) No, **(2%)**

Due to the presence of the ligands, there are different interactions among the metal electrons and the ligand electrons. **(2%)**

In this case, d_{xy}, d_{yz}, and d_{zx} have the same energy, which is lower than those of d_{z2} and d_{x2-y2}. **(2%)**

(g) For octahedral transition metal complexes with d^4, d^5, d^6, and d^7 electron configurations, there are high-spin and low-spin arrangements of the electrons. **(2%)**

These are determined by the stability gained by having maximum parallel spins, which is the case of high-spin, versus the investment in energy required to promote electrons from lower energy d_{xy}, d_{yz}, and d_{zx} to higher energy d_{z2} and d_{x2-y2} orbitals. **(2%)**

When the energy requirement is large, it favors the case of low-spin with maximum paired electrons. **(2%)**

(h) One electron in each one of the d orbitals. **(2%)**

(i) 5 **(2%)**

(j) paramagnetic **(2%)**

(k) 2 **(2%)**

(l) bromide < ammonia < carbon monoxide or $Br^- < NH_3 < CO$ **(2%)**

6. **(a) 3% ; (b) 3%**

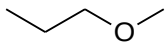
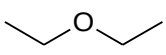
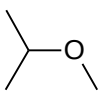
(a) 356.8 mg of CO_2 = 8.11 mmol of CO_2 ; 182.4 mg of H_2O = 10.1 mmol of H_2O

in 150 mg of X containing 97.3 mg of C and 20.2 mg H ➔ 32.5 mg of O

➔ the emperical formula of X = $C_4H_{10}O$

(b) molar mass: 50~120 g/mol ➔ X = $C_4H_{10}O$

not react with Na and not mixable with water ➔ X is an ether

X =  or  or 

7. **各 1%，共 6%**

(a) incorrect ; (b) correct ; (c) incorrect ; (d) incorrect ; (e) correct ; (f) correct

8. **各 1%，共 5%**

(a) correct ; (b) incorrect ; (c) incorrect ; (d) correct ; (e) incorrect

9. **各 2%**

(a) (p.818) two molecules are joined together **(分段給分：1%)** and a small molecule, usually water, is eliminated **(分段給分：1%)**

(b) 例如　carboxylic acid + alcohol → ester + water

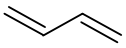
carboxylic acid + amine → amide + water

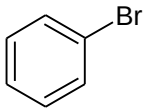
alcohol + H_2SO_4 catalyst → ether + water　　合理即可

10. **3%**

Gly-Ala-Phe-Glu-His-Gly-Ala-Leu-Val

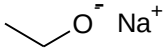
11. **共 16%**

(a)  **2%**

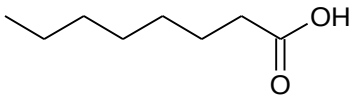
(b) 

+ HBr

(C) (substitution)　**各 2%**

(c) 

+ 1/2 H_2　**各 2%**

(d) 

+ CH_3–OH　**各 2%**