Code:	Name:

Total Scores: 38 points

	1-1	*1-2*	*1-3*	*1-4*	*1-5*	*1-6*	*1-7*	*1-8*	∑
Total Points	**4**	**4**	**4**	**4**	**6**	**4**	**8**	**4**	**38**
Received									

1-1

The order of the melting points is: C > B > A

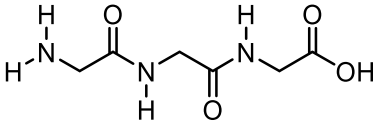
The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bondings, but not tertiary amide.

Ref. L. G. Wade, Jr., Organic Chemistry, 4^{th} ed., p. 956.

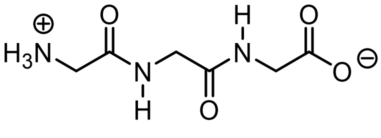
Propionamide, mp = 79 ^{o}C; *N*-methylacetamide, mp = 28 ^{o}C; *N*,*N*-dimethylformamide, mp = -61 ^{o}C.

1-2 (b) 1660 cm^{-1} due to a longer carbonyl bond length

1-3



Gly-Gly-Gly or



Gly-Gly-Gly

1-4 There are <u>27</u> possible tripeptides.

Code:	**Name:**

1-5 Among them, <u>26</u> tripeptides are optically active.

Optically inactive tripeptide: H_2N-GGG-OH

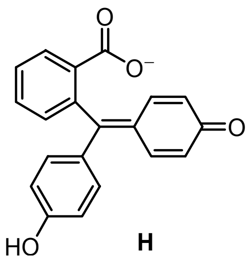
Optically active tripeptides: H_2N-GG^{L}A-OH, H_2N-GG^{D}A-OH, H_2N-G^{L}AG-OH, H_2N-^{L}AG^{D}A-OH, H_2N-^{L}A^{L}A^{D}A-OH, and so on.

1-6 The relative binding strength with polyamide gel for phenol (compound D), 4-methylphenol (compound E) and 4-nitrophenol (compound F) is: F > D > E

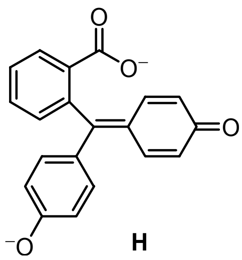
Ref. Raymond Chang Chemistry, p. 662.

K.-T. Wang J. Chin. Chem. Soc. 1959, 6, 73-79. Paper chromatography of phenols by polyamide impregnated paper.

1-7



H

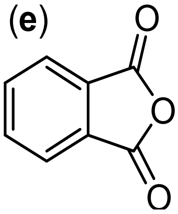


H

The acidity of phenols, J. McMurry Fundamentals of Organic Chemistry 5th ed., p. 249. The range pH 8.3-10.0 for color change of phenolphthalein.

1-8

(**e**)

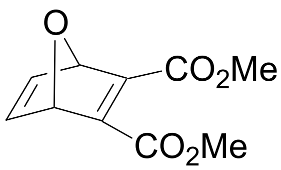


Ref. J. Chem. Soc. 1920, 117, 215. J. Med. Chem. 1999, 42, 2112-2124.

Code:	Name:

	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	∑
Total Points	4	8	6	6	6	8	6	4	48
Received									

2-1



Ref. J. Org. Chem. 1982, 47, 140-142.

2-2

T or F

__T__ (a) *OsO_4 is an oxidizing agent in the reaction of <u>A</u> to <u>B</u>.*

__T__ (b) *MeOH is generated as a by-product in the reaction of <u>B</u> to <u>C</u>.*

__T__ (c) *Protons act as the catalyst in the transformation of <u>B</u> to <u>C</u>.*

__T__ (d) *<u>C</u> will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$*

2-3

12.1 : 87.9 or 12.2 : 87.8

Ref. Tetrahedron 1984, 145.

Code:	Name:

2-4

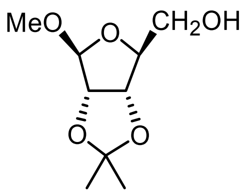
T or F

__*T*__ (a) *The reaction was to oxidize compound F.*

__*T*__ (b) *The oxygen atom inserted originated from MCPBA.*

__*F*__ (c) *The R/S notation of C-1 remained unchanged before and after the reaction.*

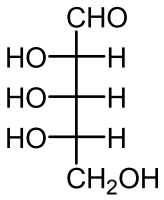
2-5



Ref. J. Org. Chem. 1990, *55*, 3853-3857 (^{1}H NMR data).

2-6 ***C-1: __S__; C-2: __S__; C-3: __R__; C-4: __S__.***

2-7



OH group for P, R and T, and H atom for Q, S and U.

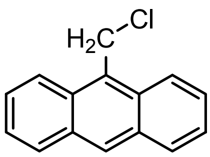
No points at all if all the P, Q, R, S, T and U are assigned to OH group. No points at all if all the P, Q, R, S, T and U are assigned to H atom.

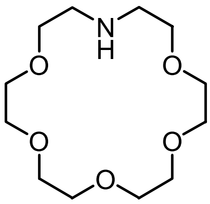
2-8 2^5

Code:	**Name:**

	3-1	*3-2*	*3-3*	*3-4*	*3-5*	*3-6*	*3-7*	*3-8*	∑
Total Points	**8**	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**36**
Received									

3-1

C: 

D: 

3-2

(d) all of them

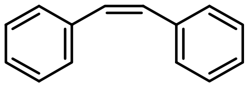
3-3

(a) **E**

3-4

(a) sodium acetate

3-5

H: 

Code:	Name:

3-6

trans

3-7 (b)

<u>K</u>

3-8

(b) C-3

Code:	Name:

	4A-1	*4A-2*	*4A-3*	*4A-4*	*4A-5*	*4A-6*	*4B-1*	*4B-2*	*4B-3*	*4B-4*	*4B-5*	∑
Total Points	**2**	**4**	**4**	**2**	**6**	**2**	**2**	**2**	**2**	**8**	**8**	**42**
Received												

4A-1

$$[\mathrm{N{\equiv}C{-}Au{-}C{\equiv}N}]^-$$

The structure of $Au(CN)_2^-$ is linear.

4A-2 13.024 g

<u>Calculation:</u>

$$4\ Au + 8\ KCN + O_2 + 2\ H_2O \rightleftharpoons 4\ KAu(CN)_2 + 4\ KOH$$

20 g ÷ 197 g/mol ≈ 0.10 mol (Au)

0.10 mol × (8/4) × 65.12 g/mol = 13.024 g (KCN)

4A-3

Oxidation $Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$

Reduction $3\ NO_3^-(aq) + 6\ H^+(aq) + 3\ e^- \rightarrow 3\ NO_2(g) + 3\ H_2O(l)$

$$Au(s) + 3\ NO_3^-(aq) + 6\ H^+(aq) + 4\ Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + 3\ NO_2(g) + 3\ H_2O(l)$$

Code:	Name:

4A-4 oxidizing agent: HNO_3 or nitric acid

reducing agent: Au

4A-5

K = $10^{25.42}$ = 2.6 $\times 10^{25}$

<u>Calculation:</u>

$$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \qquad E^o = +1.50\ V$$
$$Au(s) + 4\,Cl^-(aq) \longrightarrow AuCl_4^-(aq) + 3\,e^- \qquad -E^o = -1.00\ V$$

$$\overbrace{Au(s) + Au^{3+}(aq) + 4\,Cl^-(aq) \longrightarrow AuCl_4^-(aq) + Au(s)}^{-\,3\,e^-}_{+\,3\,e^-} \qquad E^o = +0.50\ V$$

E = E$^\circ$ − (0.059 / n) logQ

at equilibrium, Q = K, E = 0, K = $[AuCl_4^-] / [Au^{3+}] [Cl^-]^4$

E$^\circ$ = (0.059 / n) logK, 0.50 = (0.059 / 3) logK, K = $10^{25.42}$ = 2.6 $\times 10^{25}$

$\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$(-nFE_1^\circ) + (-nFE_2^\circ) = -RT\ln K$

$E^\circ = (RT/nF)\ln K = (0.059/n)\log K$, 0.50 = (0.059/3)log$K$, $K = 10^{25.42} = 2.6 \times 10^{25}$

4A-6 *Answer for multiple choice question:* **(c)**

Code:	**Name:**

4B-1 *Answer for multiple choice question:* (b)

4B-2 *Answer for multiple choice question:* (b)

4B-3 *Answer for multiple choice question:* (a)

4B-4 *Answer for multiple choice question:* (b) 10^3

Calculation:

$$\because V_{AuNPs} = \frac{4}{3} \times \pi \times r_{AuNPs}^3$$

$$V_{Au} = \frac{4}{3} \times \pi \times r_{Au}^3$$

$$\therefore N_{Au} = \frac{V_{AuNPs}}{V_{Au}} = \frac{\frac{4}{3} \times \pi \times r_{AuNPs}^3}{\frac{4}{3} \times \pi \times r_{Au}^3} = \left(\frac{r_{AuNPs}}{r_{Au}} \right)^3 = \left(\frac{15\,\mathring{A}}{1.44\,\mathring{A}} \right)^3 \approx 1000$$

Code:	Name:

4B-5 *Answer for multiple choice question:* (b) 40-50%

<u>Calculation:</u>

Method 1:

$4/3 \times \pi \times r_{AuNPs}^3 = 4/3 \times \pi \times r_{Au}^3 \times N_{Au}$ $\quad \therefore\ r_{AuNPs}^3 = r_{Au}^3 \times N_{Au}$

Surface area of a gold nanoparticle: $S_{AuNPs} = 4\pi\ r_{AuNPs}^2$

$\therefore\ S_{AuNPs} = 4\pi\ r_{Au}^2\ N_{Au}^{2/3}$

$N_S \approx S_{AuNPs} / \pi\ r_{Au}^2 = 4\ N_{Au}^{2/3}$

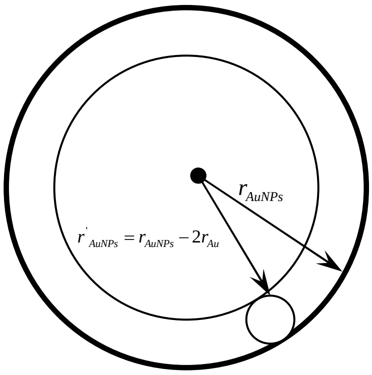
$P \approx N_S / N_{Au} = 4/ N_{Au}^{1/3}$

$N_{Au} \approx 1000$

$P \approx 40\%$

or

Method 2:

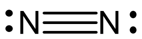
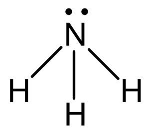
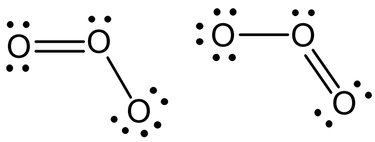


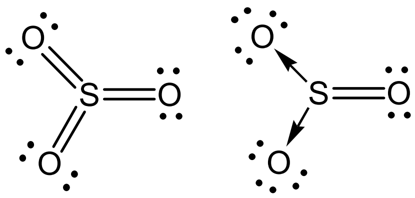
$$P\% \approx \frac{\dfrac{V_{AuNPs}}{V_{Au}} - \dfrac{V'_{AuNPs}}{V_{Au}}}{\dfrac{V_{AuNPs}}{V_{Au}}} \times 100\% = \frac{\left(\dfrac{r_{AuNPs}}{r_{Au}}\right)^3 - \left(\dfrac{r'_{AuNPs}}{r_{Au}}\right)^3}{\left(\dfrac{r_{AuNPs}}{r_{Au}}\right)^3} \times 100\% = \frac{\left(15\mathring{A}\right)^3 - \left(12.12\mathring{A}\right)^3}{\left(15\mathring{A}\right)^3} \times 100\% \approx 47\%$$

Code:	Name:

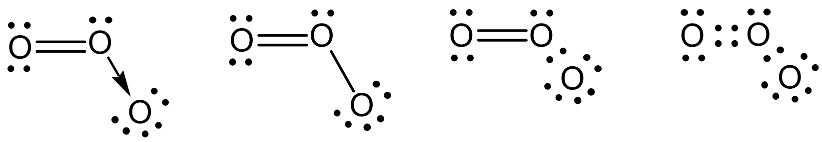
	5-1	*5-2*	*5-3*	*5-4*	*5-5*	∑
Total Points	**2**	**4**	**4**	**6**	**5**	**21**
Received						

5-1

(a)  (b)  (c) 

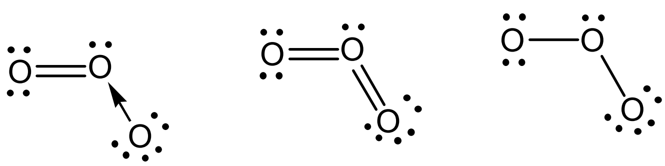
(d) 

Comment: (a) and (b) are one point each; and in (c) and (d) at least two resonance forms are required with 0.5 point for each. Dot, line and arrow sign are all correct answers.



are all correct answers

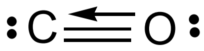
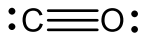
But



are incorrect answers

Code:	Name:

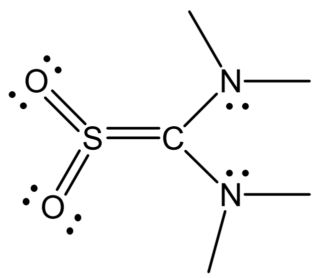
5-2

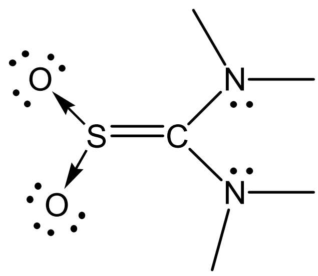
 2 points  acceptable

Formal charge C^{-1} ; O^{+1} one point (0.5 point each)

Oxidation state C^{2+} ; O^{2-} one point (0.5 point each)

5-3

The structure  is correct.

The structure  would have a formal charge and is incorrect.

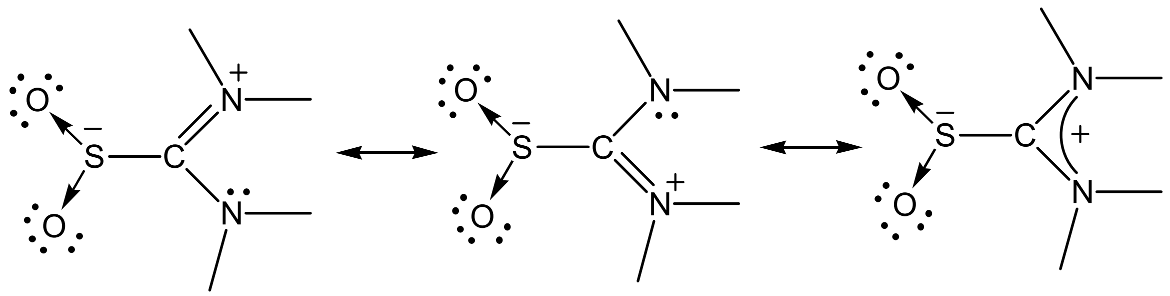
5-4 S: (b) trigonal planar (2 point)

C: (b) trigonal planar (2 point)

N: (a) trigonal pyramidal (2 point)

Code:	Name:

5-5



Lewis structure showing (1) negative charge at S, and (2) C=N double bond with positive charge at N (or related resonance form): 3 points

Resonance form showing the delocalization of C=N double bond: (1 point)

Structure showing S→O dative bond: (1 point)

Code:	Name:

	6-1	*6-2*	*6-3*	*6-4*	*6-5*	*6-6*	*6-7*	*6-8*	∑
Total Points	**4**	**4**	**6**	**6**	**4**	**6**	**6**	**4**	**40**
Received									

6-1 (4 Points)

$[H^+] = 1.00\text{x}10^{-7}$ mol/L

$K_{a1} = [HCO_3^-][H^+] / [H_2CO_3] = 2.23\text{x}10^{-4}$, $[HCO_3^-]/ [H_2CO_3] = 2.23\text{x}10^{3}$

$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69\text{x}10^{-11}$, $[CO_3^{2-}]/ [HCO_3^-] = 4.69\text{x}10^{-4}$

$\therefore$ $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}]$ = $\mathbf{4.48x10^{-4}}$: 1.00 : $\mathbf{4.69x10^{-4}}$ (4 points, 2 points for each)

(a) **(b)**

6-2 (4 Points)

$P_{CO_2} = (1.01\text{x}10^5 \text{ Pa}) \text{ x } 3.60\text{x}10^{-4} = 36.36$ Pa

$[CO_{2(aq)}] = K_{CO_2} \text{ x } P_{CO_2} = 0.0344 \text{ x } (36.36 \text{ Pa}/1.01\text{x}10^5 \text{ Pa})$ = $\mathbf{1.24x10^{-5}}$ **mol/L** (4 points)

(If you are unable to solve this problem, assume that [$CO_{2(aq)}$] = 1.11x10^{-5} M for further calculations.)

6-3(a) (6 Points)

Solubility = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$\approx [CO_{2(aq)}] + [HCO_3^-]$ (3 points)

($[H_2CO_3] = [CO_{2(aq)}] \text{ x } K_{H_2CO_3} = 2.48\text{x}10^{-8}$ mol/L and $[CO_3^{2-}] = K_{a2} / ([H^+]/[HCO_3^-]) = K_{a2} = 4.69\text{x}10^{-11}$

Code:	Name:

mol/L, both can be neglected)

$[H^+][HCO_3^-] / [CO_{2(aq)}] = K_{a1}K_{H_2CO_3} = (2.23x10^{-4})\cdot(2.00x10^{-3}) = 4.46x10^{-7}$

From ***6-2***, $[CO_{2(aq)}] = 1.24x10^{-5}$ mol/L,

$[H^+] = [HCO_3^-] = 2.35x10^{-6}$ mol/L

$\therefore$ Solubility = $[CO_{2(aq)}] + [HCO_3^-] = 1.24x10^{-5} + 2.35x10^{-6} =$ **$1.48x10^{-5}$ mol/L** (3 points)

6-3(b) (6 Points)

(Using $[CO_{2(aq)}] = 1.11x10^{-5}$ M for calculation)

Solubility = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$\approx [CO_{2(aq)}] + [HCO_3^-]$ (3 points)

(**$[H_2CO_3] = [CO_{2(aq)}] \times K_{H_2CO_3} = 2.22x10^{-8}$ mol/L** and $[CO_3^{2-}] = K_{a2} / ([H^+]/[HCO_3^-]) = K_{a2} = 4.69x10^{-11}$ mol/L, both can be neglected)

$[H^+][HCO_3^-] / [CO_{2(aq)}] = K_{a1}K_{H_2CO_3} = (2.23x10^{-4})\cdot(2.00x10^{-3}) = 4.46x10^{-7}$

From ***6-2***, **$[CO_{2(aq)}] = 1.11x10^{-5}$ mol/L,**

$[H^+] =$ **$[HCO_3^-] = 2.225x10^{-6}$ mol/L**

$\therefore$ Solubility = $[CO_{2(aq)}] + [HCO_3^-] = 1.11x10^{-5} + 2.225x10^{-6} =$ **$1.34x10^{-5}$ mol/L** (3 points)

6-4(a) (6 Points)

(Using $[CO_{2(aq)}] = 1.24x10^{-5}$ M for calculation)

Code:	Name:

In $1.00\text{x}10^{-3}$ mol/L NaOH solution, the solubility of CO_2 will be much higher because of the following reactions

(1) $CO_{2(aq)} + 2OH^- \rightleftarrows CO_3^{2-} + H_2O$ $\quad K = K_{H_2CO_3} \text{x } K_{a1} \text{x } K_{a2}/(1.00\text{x}10^{-14})^2 = 2.09\text{x}10^{11}$

(2) $CO_{2(aq)} + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^-$ $\quad K = K_{H_2CO_3} \text{ x } K_{a1}/K_{a2} = 9.37\text{x}10^3$

Combining (1) and (2): $CO_{2(aq)} + OH^- \rightleftarrows HCO_3^-$ $\quad K = 4.43\text{x}10^7$

With such a large K value, all OH^- will finally be converted to HCO_3^-.

$\therefore [HCO_3^-]$ $\quad 1.00\text{x}10^{-3}$ mol/L (4 points)

$[OH^-] = 1.82\text{x}10^{-6}$ mol/L

$[H^+] = 5.49\text{x}10^{-9}$ mol/L

$[CO_3^{2-}] = 8.54\text{x}10^{-6}$ mol/L

$\therefore$ Solubility = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

$\approx [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}] = 1.24\text{x}10^{-5} + 1.00\text{x}10^{-3} + 8.54\text{x}10^{-6} =$ $\mathbf{1.02x10^{-3}}$ **mol/L** (2 points)

6-4(b) (6 Points)

(Using $[CO_{2(aq)}] = 1.11\text{x}10^{-5}$ M for calculation)

In $1.00\text{x}10^{-3}$ mol/L NaOH solution, the solubility of CO_2 will be much higher because of the following reactions

(1) $CO_{2(aq)} + 2OH^- \rightleftarrows CO_3^{2-} + H_2O$ $\quad K = K_{H_2CO_3} \text{x } K_{a1} \text{x } K_{a2}/(1.00\text{x}10^{-14})^2 = 2.09\text{x}10^{11}$

(2) $CO_{2(aq)} + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^-$ $\quad K = K_{H_2CO_3} \text{ x } K_{a1}/K_{a2} = 9.37\text{x}10^3$

Combining (1) and (2): $CO_{2(aq)} + OH^- \rightleftarrows HCO_3^-$ $\quad K = 4.43\text{x}10^7$

With such a large K value, all OH^- will finally be converted to HCO_3^-.

Code:	Name:

∴ $[HCO_3^-]$ 1.00×10^{-3} mol/L (4 points)

$[OH^-] = 1.82 \times 10^{-6}$ mol/L

$[H^+] = 5.49 \times 10^{-9}$ mol/L

$[CO_3^{2-}] = 8.54 \times 10^{-6}$ mol/L

∴ Solubility = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

≈ $[CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}] = 1.11 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} =$ **1.02×10^{-3} mol/L** (2 points)

6-5 (4 Points)

$K_{eq} = K_{sp} \times K_{H_2CO_3} \times K_{a1}/K_{a2} = (4.50 \times 10^{-9}) \times (2.00 \times 10^{-3}) \times (2.23 \times 10^{-4})/(4.69 \times 10^{-11}) =$ **4.28×10^{-5}**

(4 points)

(If you are unable to solve this problem, assume that $K_{eq} = 5.00 \times 10^{-5}$ for further calculations.)

6-6(a) (6 Points)

(Using $K_{eq} = 4.28 \times 10^{-5}$ and $[CO_{2(aq)}] = 1.24 \times 10^{-5}$ M for calculation)

Mass balance： $[HCO_3^-] = 2[Ca^{2+}]$ (3 points)

From ***6-5***, $K = 4.28 \times 10^{-5} = [Ca^{2+}][HCO_3^-]^2/[CO_{2(aq)}] = [Ca^{2+}](2[Ca^{2+}])^2 / [CO_{2(aq)}]$

From ***6-2***, $[CO_{2(aq)}] = 1.24 \times 10^{-5}$ mol/L,

∴ $[Ca^{2+}] = 0.510 \times 10^{-3}$ mol/L = **20.5 mg/L** (3 points)

6-6(b) (6 Points)

Code:	**Name:**

(Using K_{eq} = 5.00x10^{-5} and [$CO_{2(aq)}$] = 1.11x10^{-5} M for calculation)

Mass balance： [HCO_3^-] = 2[Ca^{2+}] (3 points)

From ***6-5***, K = 5.00x10^{-5} = [Ca^{2+}][HCO_3^-]^2/[$CO_{2(aq)}$] = [Ca^{2+}](2[Ca^{2+}])^2 / [$CO_{2(aq)}$]

From ***6-2***, [$CO_{2(aq)}$] = 1.11x10^{-5} mol/L,

∴ [Ca^{2+}] = 0.5177x10^{-3} mol/L = **20.75mg/L** (3 points)

6-6(c) (6 Points)

(Using K_{eq} = 5.00x10^{-5} and [$CO_{2(aq)}$] = 1.24x10^{-5} M for calculation)

Mass balance： [HCO_3^-] = 2[Ca^{2+}] (3 points)

From ***6-5***, K = 5.00x10^{-5} = [Ca^{2+}][HCO_3^-]^2/[$CO_{2(aq)}$] = [Ca^{2+}](2[Ca^{2+}])^2 / [$CO_{2(aq)}$]

From ***6-2***, [$CO_{2(aq)}$] = 1.24x10^{-5} mol/L,

∴ [Ca^{2+}] = 0.5372x10^{-3} mol/L = **21.53 mg/L** (3 points)

6-6(d) (6 Points)

(Using K_{eq} = 4.28x10^{-5} and [$CO_{2(aq)}$] = 1.11x10^{-5} M for calculation)

Mass balance： [HCO_3^-] = 2[Ca^{2+}] (3 points)

From ***6-5***, K = 4.28x10^{-5} = [Ca^{2+}][HCO_3^-]^2/[$CO_{2(aq)}$] = [Ca^{2+}](2[Ca^{2+}])^2 / [$CO_{2(aq)}$]

From ***6-2***, [$CO_{2(aq)}$] = 1.11x10^{-5} mol/L,

∴ [Ca^{2+}] = 0.4916x10^{-3} mol/L = **19.70 mg/L** (3 points)

(If you are unable to solve this problem, assume that [Ca^{2+}]$_{(aq)}$ = 40.1 mg/L for further calculations.)

6-7 (6 Points)

Code:	Name:

HCO_3^- is the major species in solution.

The pH of the solution can be estimated as pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33)/2 = 6.99 ≈ 7.00,

where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3.

At pH 7.00, both $[OH^-]$ and $[H^+]$ can be neglected. Besides, $[CO_3^{2-}] << [HCO_3^-]$ (from ***6-1***)

Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \approx [HCO_3^-]$ (3 points)

From ***6-6***, mass balance, $[HCO_3^-] = 2[Ca^{2+}]$ = **(a)** 1.02x10^{-3} mol/L **(using $[Ca^{2+}]_{(aq)}$ from *6-6(a)*)**

(b) 1.035x10^{-3} mol/L **(using $[Ca^{2+}]_{(aq)}$ from *6-6(b)*)**

(c) 1.0744x10^{-3} mol/L **(using $[Ca^{2+}]_{(aq)}$ from *6-6(c)*)**

(d) 0.9831x10^{-3} mol/L **(using $[Ca^{2+}]_{(aq)}$ from *6-6(d)*)**

(e) 2.00x10^{-3} mol/L **(assuming $[Ca^{2+}]_{(aq)}$ = 40.1mg/L)**

∴ Alkalinity = **(a) or (b) or (c) or (d) or (e)** (3 points)

6-8(a) (4 Points)

(Using K_{eq} = 4.28x10^{-5} for calculation)

Mass balance： $[HCO_3^-] = 2[Ca^{2+}]$

$[Ca^{2+}]$ = 100 mg/L = 2.50x10^{-3} mol/L

Inserting into $K_{eq} = 4.28\text{x}10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_{2(aq)}] = 4[Ca^{2+}]^3/[CO_{2(aq)}]$

$[CO_{2(aq)}]$ = 1.46x10^{-3} mol/L (2 points)

$P_{CO_2} = ([CO_{2(aq)}] / K_{CO_2}) \times 1.01\text{x}10^5$ Pa = **4.28x10^3 Pa** (2 points)

6-8(b) (4 Points)

(Using K_{eq} = 5.00x10^{-5} for calculation)

Mass balance： $[HCO_3^-] = 2[Ca^{2+}]$

Code:	Name:

$[Ca^{2+}]$ = 100 mg/L = 2.50×10^{-3} mol/L

Inserting into $K_{eq} = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_{2(aq)}] = 4[Ca^{2+}]^3/[CO_{2(aq)}]$

$[CO_{2(aq)}] = 1.25\times10^{-3}$ mol/L (2 points)

$P_{CO_2} = ([CO_{2(aq)}] / K_{CO_2}) \times 1.01\times10^5$ Pa = **3.67×10^3 Pa** (2 points)

Code:	Name:

	7-1	*7-2*	*7-3*	*7-4*	*7-5*	∑
Total Points	**6**	**6**	**6**	***4***	***6***	**28**
Received						

7-1

$$-\frac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O][O_2] + k_2[O_3][O]$$

$$-\frac{d[O_2]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] - 2k_2[O_3][O]$$

$$-\frac{d[O]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O]$$

7-2

Equilibrium constant *K* is expressed as

$$K = \frac{[O][O_2]}{[O_3]} = \frac{k_1}{k_{-1}}$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$-\frac{d[O_3]}{dt} = k_2[O_3][O] = \frac{k_1 k_2 [O_3]^2}{k_{-1}[O_2]}$$

Code:	Name:

7-3

$$-\frac{d[O]}{dt}=0$$
$$-k_1[O_3]+k_{-1}[O][O_2]+k_2[O_3][O]=0$$

Thus $$-\frac{d[O_3]}{dt}=2k_2[O_3][O]=\frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]+k_2[O_3]}$$

7-4 $ClO_{(g)} + O_{3(g)} \rightarrow Cl_{(g)} + 2O_{2(g)}$

7-5

According to equation
k=A exp (-E_a/RT),
the ratio of rate constants yields
Ratio=exp[(14.0-2.1)x1000/(8.314x298)]=122.

Code:	Name:

	8-1	*8-2*	*8-3*	*8-4*	*8-5*	*8-7*	*8-8*	∑
Total Points	2	2	6	4	**4**	**2**	**6**	**26**
Received								

8-*1* ***Ans:*** 1

8-*2* ***Ans:*** 0 kJ/mol

8-*3*

$$f_U = \frac{C_U^{eq}}{C_N^{eq} + C_U^{eq}} = \frac{C_U^{eq}/C_N^{eq}}{1 + C_U^{eq}/C_N^{eq}} = \frac{K}{1 + K}$$

8-*4* (c) Positive below $T_{½}$, but negative above $T_{½}$

8-*5* (d) Decreases above $T_{½}$, but increases below $T_{½}$

Code:	**Name:**

8-6 *Ans:* $K = k_f / k_b$

8-7 **Ans: $dC_u/dt = -(k_f + k_b)\,[C_u - (C_u)_{eq}]$**

Show your work here

$dC_U/dt = k_f C_N - k_b C_U$

$= k_f(C - C_U) - k_b C_U = k_f C - k_f C_U - k_b C_U = k_f C - (k_f + k_b) C_U$ (1)

$K = k_f/k_b = (C_U)_{eq}/(C_N)_{eq}$

$1/K = k_b/k_f = (C_N)_{eq}/(C_U)_{eq}$

$\equiv> \quad k_b/k_f + 1 = (C_N)_{eq}/(C_U)_{eq} + 1$

$\equiv> \quad (k_b + k_f)/k_f = [(C_N)_{eq} + (C_U)_{eq}]/(C_U)_{eq}$

$\equiv> \quad (k_b + k_f)/k_f = C/(C_U)_{eq}$

$C = [(k_b + k_f)\,(C_U)_{eq}]/\,k_f$ (2)

Now substitute C obtained from eq2 to eq1.

We get $k_f\{[(k_b + k_f)\,(C_U)_{eq}]/\,k_f\} - (k_f + k_b) C_U$

$\equiv> \quad [(k_b + k_f)\,(C_U)_{eq}] - (k_f + k_b) C_U$

$\equiv> \quad -(k_f + k_b)\,[C_U - (C_U)_{eq}]$

So we get

$dC_U/dt = -(k_f + k_b)\,[C_U - (C_U)_{eq}]$