

<b>Code:</b>	<b>Name:</b>
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**Total Scores: 38 points**

	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8	$\Sigma$
<b>Total Points</b>	4	4	4	4	6	4	8	4	38
<b>Received</b>									

**1-1**

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

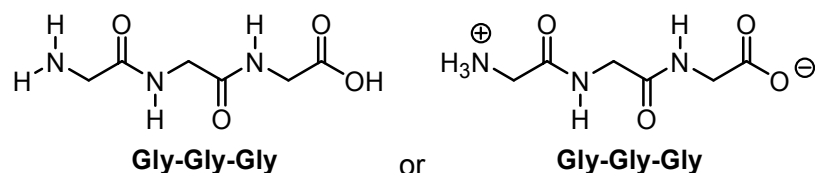
The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bondings, but not tertiary amide.

Ref. L. G. Wade, Jr., Organic Chemistry, 4<sup>th</sup> ed., p. 956.

Propionamide, mp = 79 °C; *N*-methylacetamide, mp = 28 °C; *N,N*-dimethylformamide, mp = -61 °C.

**1-2** (b) 1660 cm<sup>-1</sup> due to a longer carbonyl bond length

**1-3**



**1-4** There are 27 possible tripeptides.

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**1-5** Among them, 26 tripeptides are optically active.

Optically inactive tripeptide:  $\text{H}_2\text{N-GGG-OH}$

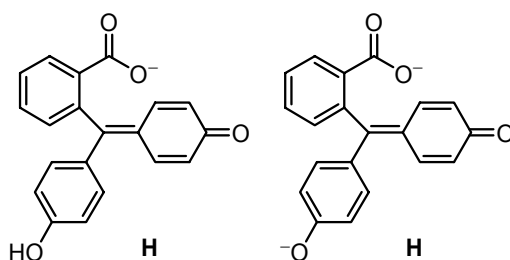
Optically active tripeptides:  $\text{H}_2\text{N-GG}^{\text{L}}\text{A-OH}$ ,  $\text{H}_2\text{N-GG}^{\text{D}}\text{A-OH}$ ,  $\text{H}_2\text{N-G}^{\text{L}}\text{AG-OH}$ ,  
 $\text{H}_2\text{N}^{\text{L}}\text{AG}^{\text{D}}\text{A-OH}$ ,  $\text{H}_2\text{N}^{\text{L}}\text{A}^{\text{L}}\text{A}^{\text{D}}\text{A-OH}$ , 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:  $\text{F} > \text{D} > \text{E}$

Ref. Raymond Chang Chemistry, p. 662.

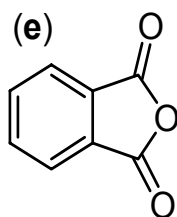
K.-T. Wang J. Chin. Chem. Soc. 1959, 6, 73-79. Paper chromatography of phenols by polyamide impregnated paper.

**1-7**



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

**1-8**

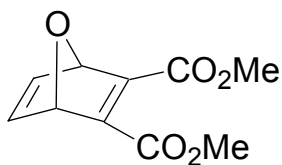


Ref. J. Chem. Soc. 1920, 117, 215. J. Med. Chem. 1999, 42, 2112-2124.

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	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	Σ
<b>Total Points</b>	4	8	6	6	6	8	6	4	48
<b>Received</b>									

**2-1**



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

**2-2**

T or F

   T (a)  $\text{OsO}_4$  is an oxidizing agent in the reaction of A to B.

   T (b) MeOH is generated as a by-product in the reaction of B to C.

   T (c) Protons act as the catalyst in the transformation of B to C.

   T (d) C will still be formed albeit in lower yields in the absence of  $\text{Me}_2\text{C}(\text{OMe})_2$

**2-3**

12.1 : 87.9 or 12.2 : 87.8

Ref. Tetrahedron 1984, 145.

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**2-4**

T or F

  T   (a) The reaction was to oxidize compound   E  .

  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 (<sup>1</sup>H NMR data).

**2-6**      C-1:   S  ; C-2:   S  ; C-3:   R  ; C-4:   S  .

**2-7**

$$\begin{array}{c}
 \text{CHO} \\
 | \\
 \text{HO} - \text{C} - \text{H} \\
 | \\
 \text{HO} - \text{C} - \text{H} \\
 | \\
 \text{HO} - \text{C} - \text{H} \\
 | \\
 \text{CH}_2\text{OH}
 \end{array}$$

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.

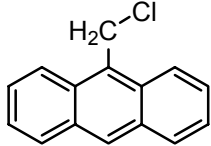
**2-8**                      2<sup>5</sup>

<b>Code:</b>	<b>Name:</b>
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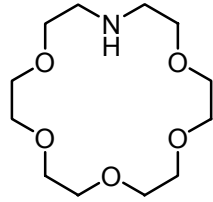
	3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8	Σ
<b>Total Points</b>	<b>8</b>	<b>4</b>	<b>4</b>	<b>4</b>	<b>4</b>	<b>4</b>	<b>4</b>	<b>4</b>	<b>36</b>
<b>Received</b>									

**3-1**

C:



D:



**3-2**

(d) all of them

**3-3**

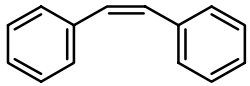
(a) E

**3-4**

(a) sodium acetate

**3-5**

H:



**Code:**

**Name:**

**3-6**

trans

**3-7 (b)**

**K**

**3-8**

(b) C-3

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	4A-1	4A-2	4A-3	4A-4	4A-5	4A-6	4B-1	4B-2	4B-3	4B-4	4B-5	Σ
<b>Total Points</b>	2	4	4	2	6	2	2	2	2	8	8	42
<b>Received</b>												

**4A-1**

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

The structure of  $\text{Au}(\text{CN})_2^-$  is linear.

**4A-2**      13.024 g

Calculation:

$$4 \text{ Au} + 8 \text{ KCN} + \text{O}_2 + 2 \text{ H}_2\text{O} \rightleftharpoons 4 \text{ KAu}(\text{CN})_2 + 4 \text{ KOH}$$

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     $\text{Au}(s) + 4 \text{ Cl}^-(aq) \longrightarrow \text{AuCl}_4^-(aq) + 3 e^-$

Reduction     $3 \text{ NO}_3^-(aq) + 6 \text{ H}^+(aq) + 3 e^- \longrightarrow 3 \text{ NO}_2(g) + 3 \text{ H}_2\text{O}(l)$

$$\text{Au}(s) + 3 \text{ NO}_3^-(aq) + 6 \text{ H}^+(aq) + 4 \text{ Cl}^-(aq) \rightleftharpoons \text{AuCl}_4^-(aq) + 3 \text{ NO}_2(g) + 3 \text{ H}_2\text{O}(l)$$

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**4A-4** oxidizing agent: HNO<sub>3</sub> or nitric acid  
 . reducing agent: Au

**4A-5**

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

Calculation:

$$\begin{array}{rcl}
 \text{Au}^{3+}(\text{aq}) + 3 \text{e}^{-} & \longrightarrow & \text{Au}(\text{s}) & E^{\circ} = +1.50 \text{ V} \\
 \text{Au}(\text{s}) + 4 \text{Cl}^{-}(\text{aq}) & \longrightarrow & \text{AuCl}_4^{-}(\text{aq}) + 3 \text{e}^{-} & -E^{\circ} = -1.00 \text{ V} \\
 \hline
 \text{Au}(\text{s}) + \text{Au}^{3+}(\text{aq}) + 4 \text{Cl}^{-}(\text{aq}) & \longrightarrow & \text{AuCl}_4^{-}(\text{aq}) + \text{Au}(\text{s}) & E^{\circ} = +0.50 \text{ V}
 \end{array}$$

$\begin{array}{c} \text{---} 3 \text{e}^{-} \text{---} \\ \text{---} 3 \text{e}^{-} \text{---} \end{array}$

$E = E^{\circ} - (0.059 / n) \log Q$

at equilibrium,  $Q = K$ ,  $E = 0$ ,  $K = [\text{AuCl}_4^{-}] / [\text{Au}^{3+}] [\text{Cl}^{-}]^4$

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

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

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

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

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



<b>Code:</b>	<b>Name:</b>
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**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:

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

Code:

Name:

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

Calculation:

Method 1:

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

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

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

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

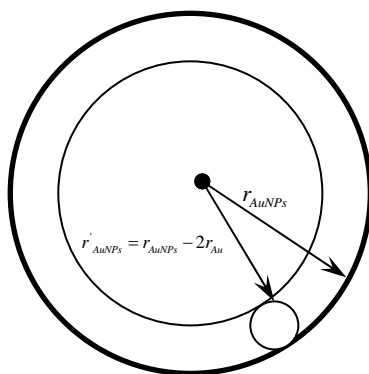
$$P \approx N_{\text{S}} / N_{\text{Au}} = 4 / N_{\text{Au}}^{1/3}$$

$$N_{\text{Au}} \approx 1000$$

$$P \approx 40\%$$

or

Method 2:

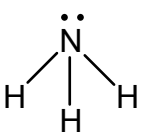
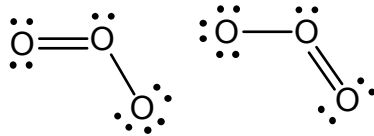


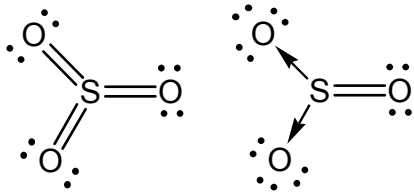
$$P\% \approx \frac{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}} - \frac{V'_{\text{AuNPs}}}{V_{\text{Au}}}}{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}}} \times 100\% = \frac{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3 - \left(\frac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3}{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3}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

<b>Code:</b>	<b>Name:</b>
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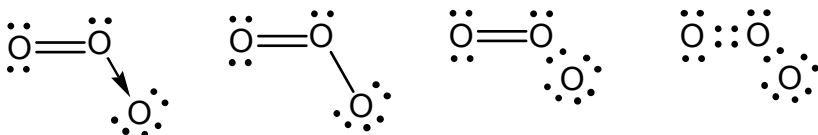
	<b>5-1</b>	<b>5-2</b>	<b>5-3</b>	<b>5-4</b>	<b>5-5</b>	$\Sigma$
<b>Total Points</b>	<b>2</b>	<b>4</b>	<b>4</b>	<b>6</b>	<b>5</b>	<b>21</b>
<b>Received</b>						

**5-1**

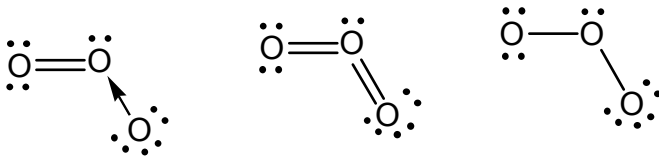
(a)  $\text{:N}\equiv\text{N:}$     (b)     (c) 

(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

<b>Code:</b>	<b>Name:</b>
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**5-2**

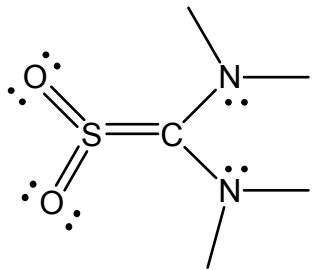
$:\text{C} \equiv \text{O}:$       2 points       $:\text{C} \equiv \text{O}:$  acceptable

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

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

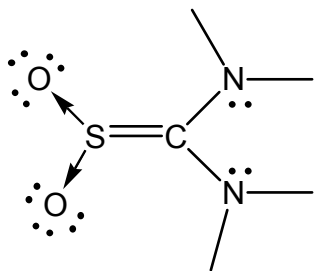
**5-3**

The structure



is correct.

The structure



would have a formal charge and is incorrect.

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

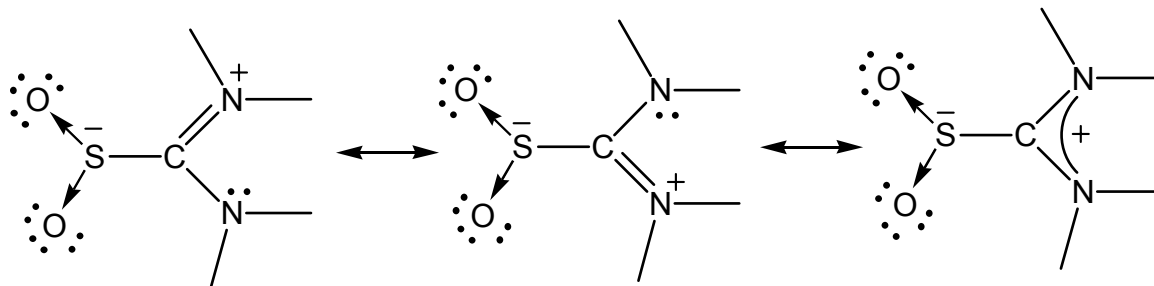
                 C: (b) trigonal planar      (2 point)

                 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)

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	<b>6-1</b>	<b>6-2</b>	<b>6-3</b>	<b>6-4</b>	<b>6-5</b>	<b>6-6</b>	<b>6-7</b>	<b>6-8</b>	$\Sigma$
<b>Total Points</b>	<b>4</b>	<b>4</b>	<b>6</b>	<b>6</b>	<b>4</b>	<b>6</b>	<b>6</b>	<b>4</b>	<b>40</b>
<b>Received</b>									

**6-1 (4 Points)**

$[H^+] = 1.00 \times 10^{-7} \text{ mol/L}$ $K_{a1} = [HCO_3^-][H^+] / [H_2CO_3] = 2.23 \times 10^{-4}$ , $[HCO_3^-] / [H_2CO_3] = 2.23 \times 10^3$ $K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69 \times 10^{-11}$ , $[CO_3^{2-}] / [HCO_3^-] = 4.69 \times 10^{-4}$ $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = 4.48 \times 10^{-4} : 1.00 : 4.69 \times 10^{-4}$ (4 points, 2 points for each) <p style="text-align: center;">(a)                      (b)</p>
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**6-2 (4 Points)**

$P_{CO_2} = (1.01 \times 10^5 \text{ Pa}) \times 3.60 \times 10^{-4} = 36.36 \text{ Pa}$ $[CO_{2(aq)}] = K_{CO_2} \times P_{CO_2} = 0.0344 \times (36.36 \text{ Pa} / 1.01 \times 10^5 \text{ Pa}) = 1.24 \times 10^{-5} \text{ mol/L}$ (4 points)
---

*(If you are unable to solve this problem, assume that  $[CO_{2(aq)}] = 1.11 \times 10^{-5} \text{ M}$  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) $[H_2CO_3] = [CO_{2(aq)}] \times K_{H_2CO_3} = 2.48 \times 10^{-8} \text{ mol/L}$ and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69 \times 10^{-11}$
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mol/L, both can be neglected)

$$[H^+][HCO_3^-] / [CO_{2(aq)}] = K_{a1}K_{H_2CO_3} = (2.23 \times 10^{-4}) \cdot (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

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

$$[H^+] = [HCO_3^-] = 2.35 \times 10^{-6}$$
 mol/L

$\therefore$  Solubility =  $[CO_{2(aq)}] + [HCO_3^-] = 1.24 \times 10^{-5} + 2.35 \times 10^{-6} = 1.48 \times 10^{-5}$  mol/L (3 points)

**6-3(b)** (6 Points)

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

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

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

$[H_2CO_3] = [CO_{2(aq)}] \times K_{H_2CO_3} = 2.22 \times 10^{-8}$  mol/L and  $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69 \times 10^{-11}$  mol/L, both can be neglected)

$$[H^+][HCO_3^-] / [CO_{2(aq)}] = K_{a1}K_{H_2CO_3} = (2.23 \times 10^{-4}) \cdot (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

From **6-2**,  $[CO_{2(aq)}] = 1.11 \times 10^{-5}$  mol/L,

$$[H^+] = [HCO_3^-] = 2.225 \times 10^{-6}$$
 mol/L

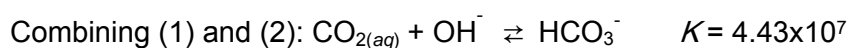
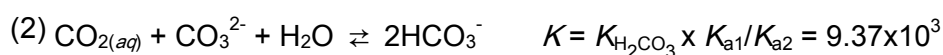
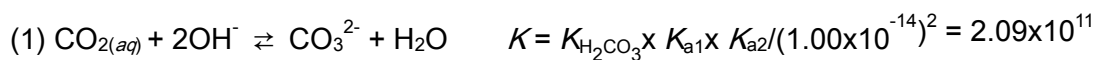
$\therefore$  Solubility =  $[CO_{2(aq)}] + [HCO_3^-] = 1.11 \times 10^{-5} + 2.225 \times 10^{-6} = 1.34 \times 10^{-5}$  mol/L (3 points)

**6-4(a)** (6 Points)

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

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In  $1.00 \times 10^{-3}$  mol/L NaOH solution, the solubility of  $\text{CO}_2$  will be much higher because of the following reactions



With such a large  $K$  value, all  $\text{OH}^-$  will finally be converted to  $\text{HCO}_3^-$ .

$$[\text{HCO}_3^-] = 1.00 \times 10^{-3} \text{ mol/L} \quad (4 \text{ points})$$

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

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

$$[\text{CO}_3^{2-}] = 8.54 \times 10^{-6} \text{ mol/L}$$

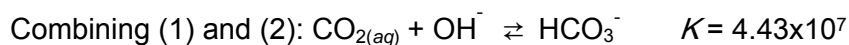
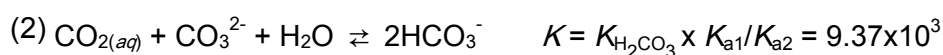
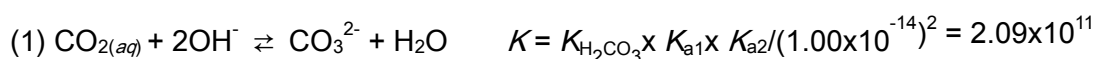
$$\text{Solubility} = [\text{CO}_{2(aq)}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\approx [\text{CO}_{2(aq)}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.24 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} = \mathbf{1.02 \times 10^{-3} \text{ mol/L}} \quad (2 \text{ points})$$

#### 6-4(b) (6 Points)

**(Using  $[\text{CO}_{2(aq)}] = 1.11 \times 10^{-5} \text{ M}$  for calculation)**

In  $1.00 \times 10^{-3}$  mol/L NaOH solution, the solubility of  $\text{CO}_2$  will be much higher because of the following reactions



With such a large  $K$  value, all  $\text{OH}^-$  will finally be converted to  $\text{HCO}_3^-$ .



<b>Code:</b>	<b>Name:</b>
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$[\text{HCO}_3^-] = 1.00 \times 10^{-3} \text{ mol/L}$ $[\text{OH}^-] = 1.82 \times 10^{-6} \text{ mol/L}$ $[\text{H}^+] = 5.49 \times 10^{-9} \text{ mol/L}$ $[\text{CO}_3^{2-}] = 8.54 \times 10^{-6} \text{ mol/L}$ Solubility = $[\text{CO}_{2(aq)}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ $\approx [\text{CO}_{2(aq)}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.11 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} = \mathbf{1.02 \times 10^{-3} \text{ mol/L}}$	(4 points)           (2 points)
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**6-5** (4 Points)

$K_{eq} = K_{sp} \times K_{\text{H}_2\text{CO}_3} \times K_{a1}/K_{a2} = (4.50 \times 10^{-9}) \times (2.00 \times 10^{-3}) \times (2.23 \times 10^{-4}) / (4.69 \times 10^{-11}) = \mathbf{4.28 \times 10^{-5}}$	(4 points)
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*(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)

<b>(Using <math>K_{eq} = 4.28 \times 10^{-5}</math> and <math>[\text{CO}_{2(aq)}] = 1.24 \times 10^{-5} \text{ M}</math> for calculation)</b>	
Mass balance : $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$	(3 points)
From <b>6-5</b> , $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_{2(aq)}] = [\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2 / [\text{CO}_{2(aq)}]$	
From <b>6-2</b> , $[\text{CO}_{2(aq)}] = 1.24 \times 10^{-5} \text{ mol/L}$ ,	
$[\text{Ca}^{2+}] = 0.510 \times 10^{-3} \text{ mol/L} = \mathbf{20.5 \text{ mg/L}}$	(3 points)

**6-6(b)** (6 Points)

<b>Code:</b>	<b>Name:</b>
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**(Using  $K_{eq} = 5.00 \times 10^{-5}$  and  $[\text{CO}_{2(aq)}] = 1.11 \times 10^{-5}$  M for calculation)**

Mass balance :  $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$  (3 points)

From **6-5**,  $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_{2(aq)}] = [\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2 / [\text{CO}_{2(aq)}]$

From **6-2**,  $[\text{CO}_{2(aq)}] = 1.11 \times 10^{-5}$  mol/L,

$[\text{Ca}^{2+}] = 0.5177 \times 10^{-3}$  mol/L = **20.75 mg/L** (3 points)

**6-6(c)** (6 Points)

**(Using  $K_{eq} = 5.00 \times 10^{-5}$  and  $[\text{CO}_{2(aq)}] = 1.24 \times 10^{-5}$  M for calculation)**

Mass balance :  $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$  (3 points)

From **6-5**,  $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_{2(aq)}] = [\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2 / [\text{CO}_{2(aq)}]$

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

$[\text{Ca}^{2+}] = 0.5372 \times 10^{-3}$  mol/L = **21.53 mg/L** (3 points)

**6-6(d)** (6 Points)

**(Using  $K_{eq} = 4.28 \times 10^{-5}$  and  $[\text{CO}_{2(aq)}] = 1.11 \times 10^{-5}$  M for calculation)**

Mass balance :  $[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$  (3 points)

From **6-5**,  $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_{2(aq)}] = [\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2 / [\text{CO}_{2(aq)}]$

From **6-2**,  $[\text{CO}_{2(aq)}] = 1.11 \times 10^{-5}$  mol/L,

$[\text{Ca}^{2+}] = 0.4916 \times 10^{-3}$  mol/L = **19.70 mg/L** (3 points)

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

**6-7** (6 Points)

<b>Code:</b>	<b>Name:</b>
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HCO<sub>3</sub><sup>-</sup> is the major species in solution.

The pH of the solution can be estimated as  $\text{pH} = (\text{p}K_{a1} + \text{p}K_{a2})/2 = (3.65 + 10.33)/2 = 6.99 \approx 7.00$ , where  $K_{a1}$  and  $K_{a2}$  are the dissociation constants of H<sub>2</sub>CO<sub>3</sub>.

At pH 7.00, both [OH<sup>-</sup>] and [H<sup>+</sup>] can be neglected. Besides, [CO<sub>3</sub><sup>2-</sup>] << [HCO<sub>3</sub><sup>-</sup>] (from 6-1)

Alkalinity = [HCO<sub>3</sub><sup>-</sup>] + 2[CO<sub>3</sub><sup>2-</sup>] + [OH<sup>-</sup>] - [H<sup>+</sup>] ≈ [HCO<sub>3</sub><sup>-</sup>] (3 points)

From 6-6, mass balance, [HCO<sub>3</sub><sup>-</sup>] = 2[Ca<sup>2+</sup>] = (a) 1.02x10<sup>-3</sup> mol/L (using [Ca<sup>2+</sup>]<sub>(aq)</sub> from 6-6(a))

(b) 1.035x10<sup>-3</sup> mol/L (using [Ca<sup>2+</sup>]<sub>(aq)</sub> from 6-6(b))

(c) 1.0744x10<sup>-3</sup> mol/L (using [Ca<sup>2+</sup>]<sub>(aq)</sub> from 6-6(c))

(d) 0.9831x10<sup>-3</sup> mol/L (using [Ca<sup>2+</sup>]<sub>(aq)</sub> from 6-6(d))

(e) 2.00x10<sup>-3</sup> mol/L (assuming [Ca<sup>2+</sup>]<sub>(aq)</sub> = 40.1mg/L)

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

**6-8(a)** (4 Points)

(Using  $K_{\text{eq}} = 4.28 \times 10^{-5}$  for calculation)

Mass balance : [HCO<sub>3</sub><sup>-</sup>] = 2[Ca<sup>2+</sup>]

[Ca<sup>2+</sup>] = 100 mg/L = 2.50x10<sup>-3</sup> mol/L

Inserting into  $K_{\text{eq}} = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_{2(aq)}] = 4[\text{Ca}^{2+}]^3 / [\text{CO}_{2(aq)}]$

[CO<sub>2(aq)}</sub>] = 1.46x10<sup>-3</sup> mol/L (2 points)

$P_{\text{CO}_2} = ([\text{CO}_{2(aq)}] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 4.28 \times 10^3 \text{ Pa}$  (2 points)

**6-8(b)** (4 Points)

(Using  $K_{\text{eq}} = 5.00 \times 10^{-5}$  for calculation)

Mass balance : [HCO<sub>3</sub><sup>-</sup>] = 2[Ca<sup>2+</sup>]

<b>Code:</b>	<b>Name:</b>
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$$[\text{Ca}^{2+}] = 100 \text{ mg/L} = 2.50 \times 10^{-3} \text{ mol/L}$$

$$\text{Inserting into } K_{\text{eq}} = 5.00 \times 10^{-5} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_{2(\text{aq})}]} = 4[\text{Ca}^{2+}]^3/[\text{CO}_{2(\text{aq})}]$$

$$[\text{CO}_{2(\text{aq})}] = 1.25 \times 10^{-3} \text{ mol/L}$$

(2 points)

$$P_{\text{CO}_2} = ([\text{CO}_{2(\text{aq})}] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = \mathbf{3.67 \times 10^3 \text{ Pa}}$$

(2 points)

<b>Code:</b>	<b>Name:</b>
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	<b>7-1</b>	<b>7-2</b>	<b>7-3</b>	<b>7-4</b>	<b>7-5</b>	$\Sigma$
<b>Total Points</b>	<b>6</b>	<b>6</b>	<b>6</b>	<b>4</b>	<b>6</b>	<b>28</b>
<b>Received</b>						

**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:**

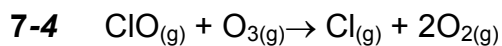
**Name:**

**7-3**

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

Thus

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



**7-5**

According to equation

$$k = A \exp(-E_a/RT),$$

the ratio of rate constants yields

$$\text{Ratio} = \exp[(14.0 - 2.1) \times 1000 / (8.314 \times 298)] = 122.$$

<b>Code:</b>	<b>Name:</b>
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	<b>8-1</b>	<b>8-2</b>	<b>8-3</b>	<b>8-4</b>	<b>8-5</b>	<b>8-7</b>	<b>8-8</b>	$\Sigma$
<b>Total Points</b>	2	2	6	4	4	2	6	26
<b>Received</b>								

**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  $T_{1/2}$ , but negative above  $T_{1/2}$

**8-5**    (d) Decreases above  $T_{1/2}$ , but increases below  $T_{1/2}$

<b>Code:</b>	<b>Name:</b>
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**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

$$dC_U/dt = k_f C_N - k_b C_U$$

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

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

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

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

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

$$\Rightarrow (k_b + k_f)/k_f = C/(C_U)_{eq}$$

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

Now substitute C obtained from eq2 to eq1.

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

$$\Rightarrow [(k_b + k_f) (C_U)_{eq}] - (k_f + k_b)C_U$$

$$\Rightarrow - (k_f + k_b) [C_U - (C_U)_{eq}]$$

So we get

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