# 2024 SPRING Semester Mid-term Examination <br> For General Chemistry I 

Date: April 17(Wed), Time Limit: 19:00~21:00

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

| Professor Name | Class | Student I.D. Number | Name |
| :--- | :--- | :--- | :---: |
|  |  |  |  |


| Problem | points | Problem | points | TOTAL pts |
| :---: | ---: | :---: | ---: | :--- |
| $\mathbf{1}$ | $/ 15$ | $\mathbf{6}$ | $/ 8$ |  |
| $\mathbf{2}$ | 18 | $\mathbf{7}$ | 110 |  |
| $\mathbf{3}$ | $/ 8$ | $\mathbf{8}$ | $/ 16$ |  |
| $\mathbf{4}$ | $/ 10$ | $\mathbf{9}$ | 100 |  |
| $\mathbf{5}$ | $/ 10$ |  |  |  |

** This paper consists of 21 sheets with 9 problems (page 18-20: Equation, constants \& periodic table, page 21: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer sheet. Please write down the unit of your answer when applicable. You will get $30 \%$ deduction for a missing unit.

## NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

0 Return and Claim Period: April 22 (Monday, 19:00~21:00, 2 hrs)
The claim is permitted only on this period. Keep that in mind!

0 Location: Each designated room of Creative Learning Bldg. (E11)

| Class | Room(E11) |
| :---: | :---: |
| $\mathbf{A}$ | 301 |
| $\mathbf{B}$ | 302 |
| C | 309 |
| D | 303 |

Procedure
Rule 1: Students cannot bring their writing tools into the rooms (Use a pen only provided by TA)
Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

If you have any claims on it, write them on the claim form and attach it to the top of the exam paper with a stapler. Give them to your TA.

## WARNING!!

If you deliberately alter any original answers or insert something on your marked paper to achieve a better grade, you will get a F grade for this course. Or if you don't keep the rules above, we will regard it as a kind of cheating and give you 0 point. So please don't cheat.

## 2. Final Confirmation

1) Period: April 25(Thu.) ~ 26(Fri.)
2) Procedure: During this period, you can check final score of the examination on the website again.
(No additional corrections. If no change in your score after reasoning, the claims were not accepted.)
** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr

## 1. (15 points)

Answer the following questions:
(a) (3 points) Balance the equation for this reaction in basic solution.

$$
\mathrm{S}(\mathrm{~s})+\mathrm{OCl}^{-}(\mathrm{aq}) \longrightarrow \mathrm{SO}_{3}^{2-}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})
$$

(b) (3 points) Define the term 'polarizability' and explain its significance in the context of atomic and molecular behavior.
(c) (3 points) Describe what an electrostatic potential map represents and explain the significance of the red and blue color domains in this map.
(d) (3 points) When 70.5 mg of a sample of potassium phosphate $\left(\mathrm{K}_{3} \mathrm{PO}_{4}\right)$ was added to 15.0 mL of 0.050 M silver nitrate $\left(\mathrm{AgNO}_{3}\right)$ solution, a precipitate formed. how many moles of precipitation are produced?
(e) (3 points)Arrange the following compounds in order of higher boiling points, and justify in terms of relevant intermolecular interactions. (a) n-butane; (b) ethene, (c) methane, (d) butanoic acid; (e) 1propanol.
(a)

Step 1: Write the two skeleton half-equations.

$$
\mathrm{S}(\mathrm{~s}) \rightarrow \mathrm{SO}_{3}{ }^{2-}(\mathrm{aq}) \text { and } \mathrm{OCl}^{-}(\mathrm{aq}) \rightarrow \mathrm{Cl}^{-}(\mathrm{aq})
$$

Step 2: Balance each skeleton half-equation for O (with $\mathrm{H}_{2} \mathrm{O}$ ) and for H atoms (with $\mathrm{H}^{+}$).
$3 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{S}(\mathrm{s}) \rightarrow \mathrm{SO}_{3}{ }^{2-}(\mathrm{aq})+6 \mathrm{H}^{+}$
$\mathrm{OCl}^{-}(\mathrm{aq})+2 \mathrm{H}^{+} \rightarrow \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
Step 3: Balance electric charge by adding electrons.
$3 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{S}(\mathrm{s}) \rightarrow \mathrm{SO}_{3}^{2-}(\mathrm{aq})+6 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-}$
$\mathrm{OCl}^{-}(\mathrm{aq})+2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
Step 4: Change from an acidic medium to a basic one by adding $\mathrm{OH}^{-}$to eliminate $\mathrm{H}^{+}$.
$3 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{S}(\mathrm{s})+6 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{SO}_{3}{ }^{2-}(\mathrm{aq})+6 \mathrm{H}^{+}(\mathrm{aq})+6 \mathrm{OH}^{-}(\mathrm{aq})+4 \mathrm{e}^{-}$
$\mathrm{OCl}^{-}(\mathrm{aq})+2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{OH}^{-}(\mathrm{aq})$
Step 5: Simplify by removing the items present on both sides of each halfequation, and combine the half-equations to obtain the net redox equation.
Oxidation: $\mathrm{S}(\mathrm{s})+6 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{SO}_{3}{ }^{2-}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+4 \mathrm{e}^{-}$

Reduction: $\left\{\mathrm{OCl}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})\right\} \times 2$

Overall: $\mathrm{S}(\mathrm{s})+6 \mathrm{OH}^{-}(\mathrm{aq})+2 \mathrm{OCl}^{-}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{SO}_{3}^{2-}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{Cl}^{-}(\mathrm{aq})+4 \mathrm{OH}^{-}$
Simplify by removing the species present on both sides.
Net ionic equation: $\mathrm{S}(\mathrm{s})+2 \mathrm{OH}^{-}(\mathrm{aq})+2 \mathrm{OCl}^{-}(\mathrm{aq}) \rightarrow \mathrm{SO}_{3}{ }^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{Cl}^{-}(\mathrm{aq})$
(b) The polarizability provides a measure of the extent to which an electron cloud can be distorted by the application of an electric field or the approach of another molecule.

Polarizability increases with the size of the atom.
(c) The electrostatic potential map is obtained by hypothetically probing an electron density surface with a positive point charge. The positive point charge will be attracted to an electron-rich region-a region of excess negative charge when all the charges of the nuclei and electrons have been taken into account-and the electrostatic potential will be negative.
(d)
$\mathrm{K}_{3} \mathrm{PO}_{4}(\mathrm{aq})+3 \mathrm{AgNO}_{3}(\mathrm{aq}) \rightarrow \mathrm{Ag}_{3} \mathrm{PO}_{4}(\mathrm{~s})+3 \mathrm{KNO}_{3}(\mathrm{aq})$
$\mathrm{K}_{3} \mathrm{PO}_{4} 70.5 \mathrm{mg}=0.0705 / 212=0.333 \mathrm{mmol}$.
$\mathrm{AgNO}_{3}=0.050 \mathrm{Mx} 15.0 \mathrm{~mL}=0.75 \mathrm{mmol}$.
$\mathrm{K}_{3} \mathrm{PO}_{4}$ and $\mathrm{AgNO}_{3}$ react in a 1:3 ratio. Limiting reactant $=\mathrm{AgNO}_{3}$.
$\mathrm{AgNO}_{3}$ and $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ have a $3: 1$ relationship.
Precipitated $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ occurs at $1 / 3(\mathrm{~mol})$ of the occurrence of $\mathrm{AgNO}_{3}$
i.e. 0.25 mmol
(e) in order of increasing boiling points: Methane $<$ Ethene $<$ n-Butane $<1$-Propanol $<$ Butanoic Acid. The key determining factors are the types and strengths of intermolecular interactions: London dispersion forces, dipole-dipole interactions, and hydrogen bonding.

## 2 (8 points)

$\mathrm{CCl}_{4}$, an important commercial solvent, is prepared by the reaction of $\mathrm{Cl}_{2}(\mathrm{~g})$ with a carbon compound.
Determine $\Delta_{\mathrm{r}} H^{\circ}$ for the reaction

$$
\mathrm{CS}_{2}(\mathrm{l})+3 \mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{CCl}_{4}(\mathrm{l})+\mathrm{S}_{2} \mathrm{Cl}_{2}(\mathrm{l}) \quad \Delta_{r} H^{\circ}=?
$$

Use appropriate data from the following listing.

$$
\begin{gathered}
\mathrm{CS}_{2}(\mathrm{l})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{SO}_{2}(\mathrm{~g}) \quad \Delta_{r} H_{1}^{\circ}=-1077 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
2 \mathrm{~S}(\mathrm{~s})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{S}_{2} \mathrm{Cl}_{2}(\mathrm{~g}) \quad \Delta_{r} H_{2}^{\circ}=-58.2 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\mathrm{C}(\mathrm{~s})+2 \mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{CCl}_{4}(\mathrm{l}) \quad \Delta_{r} H_{3}{ }^{\circ}=-135.4 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\mathrm{~S}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{SO}_{2}(\mathrm{~g}) \quad \Delta_{r} H_{4}^{\circ}=-296.8 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta_{r} H_{5}{ }^{\circ}=-393.5 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{gathered}
$$

First, we can see that we are able to get the necessary reactants by combining first three reactions.
$\mathrm{CS}_{2}+3 \mathrm{O}_{2}+\mathrm{C}+3 \mathrm{Cl}_{2}+2 \mathrm{~S} \rightarrow \mathrm{CO}_{2}+\mathrm{CCl}_{4}+\mathrm{S}_{2} \mathrm{Cl}_{2}+2 \mathrm{SO}_{2}$ ( 3 points)
However, this reaction has chemical species that need to be eliminated: $\mathrm{O}_{2}, \mathrm{C}, 2 \mathrm{~S}, \mathrm{CO}_{2}$, and $\mathrm{SO}_{2}$.
Using the last two reactions, all of these chemical species could be eliminated.
Therefore,

$$
\Delta_{r} H^{\circ}=\Delta_{\mathrm{r}} H_{1}{ }^{\circ}+\Delta_{\mathrm{r}} H_{2}{ }^{\circ}+\Delta_{\mathrm{r}} H_{3}{ }^{\circ}-2 \times \Delta_{\mathrm{r}} H_{4}{ }^{\circ}-\Delta_{\mathrm{r}} H_{5}{ }^{\circ}
$$

$=-284 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (5 ponts)

## 3. (8 points)

Consider a scenario where an electron is removed from a fluorine molecule, resulting in the formation of an $\mathrm{F}_{2}{ }^{+}$molecular ion.
(a) (2 points) Provide the molecular electron configurations for both $\mathrm{F}_{2}$ and $\mathrm{F}_{2}{ }^{+}$.
(b) ( 2 points) Determine and state the bond order for each species, $\mathrm{F}_{2}$ and $\mathrm{F}_{2}{ }^{+}$.
(c) (2 points) Based on the electron configurations, identify which species $\left(\mathrm{F}_{2}\right.$ or $\mathrm{F}_{2}{ }^{+}$) is expected to be paramagnetic.
(d) (2 points) Using your understanding of molecular structure and bonding, predict which species, $\mathrm{F}_{2}$ or $\mathrm{F}_{2}{ }^{+}$, possesses higher bond dissociation energy.

## Answer

(a) (2 pts)
$\mathrm{F}_{2}$ is a homonuclear diatomic molecule, which has 18 electrons of which 14 are valence electrons. The $\mathrm{F}_{2}{ }^{+}$ion has lost a valence electron and so has 13 . Based on the correlation diagram for $\mathrm{F}_{2}$, the energetic order can be obtained like the following.
$\mathrm{F}_{2}\left(\sigma_{2 \mathrm{~s}}\right)^{2}\left(\sigma^{*}{ }_{2 \mathrm{~s}}\right)^{2}\left(\sigma_{2 \mathrm{p}}\right)^{2}\left(\pi_{2 \mathrm{p}}\right)^{4}\left(\pi^{*}{ }_{2 \mathrm{p}}\right)^{4}$
$\mathrm{F}_{2}{ }^{+}\left(\sigma_{2 \mathrm{~s}}\right)^{2}\left(\sigma^{*}{ }_{2 \mathrm{~s}}\right)^{2}\left(\sigma_{2 \mathrm{p}}\right)^{2}\left(\pi_{2 \mathrm{p}}\right)^{4}\left(\pi^{*}{ }_{2 \mathrm{p}}\right)^{3}$
(b) ( 2 pts ) The $\mathrm{F}_{2}$ molecule has two more bonding than antibonding electrons. Its order is $1 ; \mathrm{F}_{2}{ }^{+}$ion has three more bonding than antibonding electrons. Its bonding order is $3 / 2$.
(c) ( 2 pts ) The $\mathrm{F}_{2}$ molecule has zero unpaired electrons. Accordingly, $\mathrm{F}_{2}$ is diamagnetic. The $\mathrm{F}_{2}{ }^{+}$ion has an odd number of electrons. Because at least one electron (a $\pi^{*}{ }_{2 p}$ electron) is unpaired. So, $\mathrm{F}_{2}{ }^{+}$ion is paramagnetic.
(d) (2 pts) The $\mathrm{F}_{2}{ }^{+}$ion has a larger bond order and therefore requires more energy to dissociate than $\mathrm{F}_{2}{ }^{+}$ion's case.

## 4. (10 points)

Maxwell-Boltzmann distribution of speed is given by the following equation

$$
f(v)=4 \pi\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} v^{2} e^{-m v^{2} / 2 k_{B} T}
$$

Where $k_{\mathrm{B}}$ is Boltzmann constant, $T$ is temperature, and v is the speed.
(a) (4 points) Show that the root-mean-square speed ( $u_{r m s}$ ) is larger than the most probable speed ( $\mathrm{u}_{\mathrm{m}}$ ).
(b) (3 points) Calculate the ratio of rms speed of $\mathrm{H}_{2}$ to that of $\mathrm{N}_{2}$ at room temperature $\left(\mathrm{v}_{\mathrm{rms}}, \mathrm{H}_{2} / \mathrm{v}_{\mathrm{rms}}\right.$, $\mathrm{N}_{2}$ ).
(c) (3 points) Calculate the ratio of rms speed of $\mathrm{H}_{2}$ at $273{ }^{\circ} \mathrm{C}$ to that of $\mathrm{H}_{2}$ at $0^{\circ} \mathrm{C}\left(\mathrm{v}_{\mathrm{rms}}\right.$ at $273{ }^{\circ} \mathrm{C} / \mathrm{v}_{\mathrm{rm}}$ at $0^{\circ} 0^{\circ} \mathrm{C}$.

Answer: (a)
Most probable speed:

$$
v_{m p}=\sqrt{\frac{2 k_{B} T}{m}}=\sqrt{\frac{2 R T}{M}} \quad\left[\frac{d f(v)}{d v}=0\right]_{v=v_{m p}}
$$

Mean square speed:

$$
\overline{v^{2}}=\int_{0}^{\infty} v^{2} f(v) d v=\frac{3 k_{B} T}{m}=\frac{3 R T}{M}
$$

Root-mean-square speed:

$$
v_{r m s}=\sqrt{\overline{v^{2}}}=\sqrt{\frac{3 k_{B} T}{m}}=\sqrt{\frac{3 R T}{M}}
$$

So root-mean-square speed is larger than the most probable speed
(b) $v_{\text {rms }}, \mathrm{H}_{2} / \mathrm{v}_{\mathrm{rms}}, \mathrm{N}_{2}=\left(\mathrm{M}_{\mathrm{N} 2} / \mathrm{M}_{\mathrm{H} 2}\right)^{1 / 2}=14^{1 / 2}$
(c) $\mathrm{V}_{\text {rms }}$ at $273{ }^{\circ} \mathrm{C} / \mathrm{V}_{\text {rm }}$ at ${ }^{\circ} \mathrm{C}=(273+273 \mathrm{~K} / 273 \mathrm{~K})^{1 / 2}=2^{1 / 2}$

## 5. (10 points)

Answer the following questions.
(a) (2 points) Draw the most accepted Lewis (dot) structure for $\mathrm{NO}_{2}{ }^{+}$, predict its molecular shape according to the VSEPR model, and assign the appropriate hybridization for the central N atom.


Structure: +1
Hybridization: +1
(b) (3 points) Draw the most accepted Lewis (dot) structure for $\mathrm{NO}_{2}$, predict its molecular shape according to the VSEPR model, and assign the appropriate hybridization for the central N atom.

$$
\mathrm{SN}=3 \text {; bent } \rightarrow s p^{2}
$$

Structure: +1
Hybridization: +1
Resonance: +1
(c) (2 points) You have studied the delocalized $\pi$-bonding molecular orbitals for ozone in class.

Likewise, draw an energy-level diagram of the $\pi$-bonding molecular orbitals, with electrons allocated, based on the Lewis structure for $\mathrm{NO}_{2}$ proposed in (b).


Energy diagram: +1
Electrons: +1

* It is NOT needed to draw something like the left one.
(d) (3 points) Draw an energy-level diagram of the $\pi$-bonding molecular orbitals, with electrons allocated, based on the Lewis structure for $\mathrm{NO}_{2}{ }^{+}$given in (a). OR describe the bond ( $\sigma$ and $\pi$ ) characters/geometries with the hybridization concept.


All or nothing!

## 6. (8 points)

An electron is confined to a 1.2 nm one-dimensional box. Considering that visible light has a wavelength between 400 nm and 700 nm , (a) \& (b) determine whether the following transition results in the visible spectrum.
(a) (2 points) $n=2$ to $n=1$
(b) (2 points) $n=3$ to $n=1$
(c) (4 points) Suppose this electron undergoes transitions among all possible states, and several visible spectral lines are observed as a result of these transitions. How many visible spectral lines must be observed?
(a)

$$
\begin{aligned}
& E_{n}=\frac{n^{2} h^{2}}{8 m L^{2}} \\
& E_{2}-E_{1}=\left(2^{2}-1^{2}\right) \cdot \frac{h^{2}}{8 m L^{2}}=\frac{3 h^{2}}{8 m L^{2}}=\frac{3 \times\left(6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}^{-1}\right)^{2}}{8 \times\left(9.109 \times 10^{-31} \mathrm{~kg}\right) \times\left(1.2 \times 10^{-9} \mathrm{~m}\right)^{2}} \\
& =1.3 \times 10^{-19} \mathrm{~J}=h \frac{c}{\lambda} \ldots+1 \mathrm{pt} \\
& \therefore \lambda=\frac{h c}{E_{2}-E_{1}}=\frac{\left(6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}\right.}{} \frac{-1}{1.3 \times 10^{-19} \mathrm{~J}} \times\left(2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}\right) \\
&
\end{aligned}
$$

It is above 700 nm , so it does NOT result in the visible spectrum.
(b)

$$
\begin{aligned}
&\left.E_{3}-E_{1}=\left(3^{2}-1^{2}\right) \cdot \frac{h^{2}}{8 m L^{2}}=\frac{8 h^{2}}{8 m L^{2}}=\frac{8 \times\left(6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}\right.}{}{ }^{-1}\right)^{2} \\
& 8 \times\left(9.109 \times 10^{-31} \mathrm{~kg}\right) \times\left(1.2 \times 10^{-9} \mathrm{~m}\right)^{2} \\
&=3.3 \times 10^{-19} \mathrm{~J}=h \frac{c}{\lambda} \ldots+1 \mathrm{pt} \\
& \lambda=\frac{h c}{E_{2}-E_{1}}=\frac{\left(6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}^{-1}\right) \times\left(2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}\right)}{3.3 \times 10^{-19} \mathrm{~J}}=600 \mathrm{~nm} \ldots+2 \mathrm{pt}
\end{aligned}
$$

It is within the $400 \mathrm{~nm}-700 \mathrm{~nm}$ region, so it DOES result in the visible spectrum.
(c)

For any transition from $n_{i}$ to $n_{f}$ where $i>f$,

$$
\begin{aligned}
\lambda=\frac{h c}{\Delta E}=h c & \times \frac{8 m L^{2}}{\left(n_{i}^{2}-n_{f}^{2}\right) h^{2}}=\frac{8 m c L^{2}}{\left(n_{i}^{2}-n_{f}^{2}\right) h} \\
& \left.=\frac{8 \times\left(9.109 \times 10^{-31} \mathrm{~kg}\right) \times\left(2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}\right) \times\left(1.2 \times 10^{-9} \mathrm{~m}\right)^{2}}{\left(n_{i}^{2}-n_{f}^{2}\right) \times\left(6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}\right.}{ }^{-1}\right)
\end{aligned}=\frac{475 \mathrm{~nm}}{n_{i}^{2}-n_{f}^{2}}
$$

In order to fall in the visible region:

$$
\begin{gathered}
400 \mathrm{~nm}<\frac{475 \mathrm{~nm}}{n_{i}^{2}-n_{f}^{2}}<700 \mathrm{~nm} \ldots+2 \mathrm{pt} \\
6.78<n_{i}^{2}-n_{f}^{2}<11.9
\end{gathered}
$$

There are four transitions satisfying this condition: 3 to 1,4 to 3,5 to 4 , and 6 to $5 \ldots+2$ pt Therefore, four visible spectral lines must be observed.

## 7. (10 points)

Electrons in molecules are described by wavefunctions that extend over more than one atom. Consider an electron that is located in the $\pi$-bonding molecular orbital that extends over two adjacent carbon atoms in ethene. The electron can move freely between the two C atoms. The internuclear $\mathrm{C}=\mathrm{C}$ distance is 134 pm .
(1) (2 points) Using the one-dimensional particle-in-the-box model, calculate the wavelength of light that is required to promote an electron from the $n=1$ to the $n=2$ level, assuming that the length of the box is the same as the distance between the two carbon atoms. Express the wavelength in nm. >>

$$
\begin{gathered}
E_{n}=\frac{n^{2} h^{2}}{8 m L^{2}} \\
E_{2}-E_{1}=h \nu=h c / \lambda \\
\frac{6.626 \times 10^{-34} \mathrm{~m}^{2} \mathrm{~kg} \mathrm{~s}^{-1}}{8\left(9.109 \times 10^{-31} \mathrm{~kg}\right)\left(1.34 \times 10^{-10} \mathrm{~m}\right)^{2}}(4-1)=\frac{2.998 \times 10^{8} \mathrm{~m} / \mathrm{s}}{\lambda} \\
\lambda=1.97 \times 10^{-8} \mathrm{~m}=19.7 \mathrm{~nm}
\end{gathered}
$$

(2) (3 points) Let's use the same model for 1,3-butadiene $\left(\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}_{2}\right)$. Let's assume that we can ignore bond angles and find the size of the box by adding $\mathrm{C}=\mathrm{C}$ and $\mathrm{C}-\mathrm{C}$ bond lengths, which is 134 and 148 pm , respectively. Calculate the wavelength of light that can promote an electron from HOMO to LUMO.
>> Since the system has four $\pi$ electrons, HOMO and LUMO are $n=2$ and 3 levels, respectively.

$$
\begin{gathered}
\frac{6.626 \times 10^{-34} \mathrm{~m}^{2} \mathrm{~kg} \mathrm{~s}^{-1}}{8\left(9.109 \times 10^{-31} \mathrm{~kg}\right)\left((1.34 \times 2+1.48) \times 10^{-10} \mathrm{~m}\right)^{2}}(9-4)=\frac{2.998 \times 10^{8} \mathrm{~m} / \mathrm{s}}{\lambda} \\
\lambda=1.14 \times 10^{-7} \mathrm{~m}=114 \mathrm{~nm}
\end{gathered}
$$

(3) (5 points) To develop molecules that can emit visible light (400-700 nm), what are the minimum and maximum numbers of double bonds that should be included in the molecules? Assume that the molecule is linear and has the conjugated $\pi$ system such as $\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}, \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}, \mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}-$ $\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}$, and so on. Assume that the light emission is associated with the LUMO $\rightarrow$ HOMO transition.
$\gg$ As seen above, for the system that has n double bonds and thus $2 \mathrm{n} \square$ electrons, the HOMO-LUMO gap is $\mathrm{E}_{\mathrm{n}+1}-\mathrm{E}_{\mathrm{n}}$.

$$
\lambda=\frac{2.998 \times 10^{8} \mathrm{~m} / \mathrm{s}}{\frac{6.626 \times 10^{-34} \mathrm{~m}^{2} \mathrm{~kg} \mathrm{~s}^{-1}}{8\left(9.109 \times 10^{-31} \mathrm{~kg}\right)\left((1.34 n+1.48 \times(n-1)) \times 10^{-10} \mathrm{~m}\right)^{2}}(2 n+1)}
$$

For $\mathrm{n}=1, \lambda=19.7 \mathrm{~nm}$
For $\mathrm{n}=2, \lambda=114 \mathrm{~nm}$
For $\mathrm{n}=3, \lambda=229 \mathrm{~nm}$
For $\mathrm{n}=4, \lambda=352 \mathrm{~nm}$
For $\mathrm{n}=5, \lambda=477 \mathrm{~nm}$; the minimum $\#$ of $\mathrm{C}=\mathrm{C}$ bonds
For $\mathrm{n}=6, \lambda=605 \mathrm{~nm}$; the maximum $\#$ of $\mathrm{C}=\mathrm{C}$ bonds
For $\mathrm{n}=7, \lambda=733 \mathrm{~nm}$

## 8. (16 points)

To detect the presence of $\mathrm{Fe}(\mathrm{III})$, the solution of potassium thiocyanate (KSCN) can be used, because Fe-thiocyanate compounds display a blood-red color. There are two binding modes for the $\mathrm{Fe}-$ thiocyanate bond formation; N -bonding and S -bonding. To explain this phenomenon, let's consider Lewis structure for thiocyanate anion.
(1) (9 points) Draw all nine possible Lewis structures for a thiocyanate anion and write formal charges for each atom in each Lewis structure.
>>

(2) (2 points) What are the two most likely structures considering the formal charge distributions? Draw the structures for the N -bonding and S -bonding modes.
>> Structures with the least charge separation are more likely. Thus, the following two structures are the most likely structures. Considering the electronegativities of N and $\mathrm{S}, 3.0$ and 2.5 , respectively, the left structure is more stable, but they are close in energy, resulting in two Fe-binding modes.

| -1 | 0 | 0 | 0 | 0 | -1 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $-\ddot{N}$ | $=C=\ddot{S}$ | $\ddot{N}=C-\ddot{S}-:$ |  |  |  |

## N -bonding mode <br> $\mathrm{Fe}-\mathrm{N}=\mathrm{C}=\mathrm{S}$

## S-bonding mode <br> $\mathrm{N} \equiv \mathrm{C}-\mathrm{S}-\mathrm{Fe}$

(3) To generate thiocyanate ions, the following reactions can be used.
(3-1) (2 points) $8 \mathrm{CN}^{-}+\mathrm{S}_{8} \rightarrow 8 \mathrm{SCN}^{-}$(S-bonding mode structure)
Which atom of the reactants is reduced and which atom is oxidized? Use formal charge changes.
(3-2) (3 points) $\mathrm{CN}^{-}+\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-} \rightarrow \mathrm{SCN}^{-}+\mathrm{SO}_{3}{ }^{2-}$ (N-bonding mode structure)
Draw the Lewis structures of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ and $\mathrm{SO}_{3}{ }^{2-}$ ions and determine formal charges. Is this reaction a redox reaction or S atom transfer reaction? Rationalize your answer by using formal charges.
>>
(3-1) C is oxidized while S is reduced.

(3-2) As seen below, the formal charge of S does not change over the reaction. ( C and N exchange an electron within a molecule; not an inter-molecular exchange). Thus, it is a sulfur atom transfer reaction.

-1

-1

## 9. (15 points)

The photoelectron spectroscopy (PES) experiment measures the kinetic energies of electrons that are ejected from atoms by the absorption of high-energy photons. The PES studies of sodium atoms excited by X-rays with wavelength $9.890 \times 10^{-10} \mathrm{~m}$ show four peaks in which the electrons have speeds $7.992 \times 10^{6} \mathrm{~m} \mathrm{~s}^{-1}$ (peak a), $2.046 \times 10^{7} \mathrm{~m} \mathrm{~s}^{-1}\left(\right.$ peak b), $2.074 \times 10^{7} \mathrm{~m} \mathrm{~s}^{-1}($ peak c), and $2.009 \times$ $10^{7} \mathrm{~m} \mathrm{~s}^{-1}$ (peak d).
(a) (2 points) Provide the electron configuration of sodium in its ground state.
(b) (2 points) Determine the energy (in electron volts, eV ) of the X-rays utilized to irradiate sodium atoms.
(c) (4 points) Compute the kinetic energy (in eV ) for electrons corresponding to each peak.
(d) (4 points) Ascertain the ionization energy (in eV ) for electrons related to each peak.
(e) (3 points) Correlate each peak to a specific orbital in the sodium atom and illustrate the energylevel diagram of sodium based on photoelectron spectroscopy findings.
(a) The ground-state electron configuration of sodium is $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{1}$.
(b) The energy of the X-rays is

$$
\begin{gathered}
\mathrm{E}_{X-r a y}=h v=\frac{h c}{\lambda}=\frac{\left(6.62607 \times 10^{-34} \mathrm{~J} \mathrm{~s}\right)\left(2.99792 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}\right)}{9.890 \times 10^{-10} \mathrm{~m}}=2.0085 \times 10^{-16} \mathrm{~J} \\
\\
=2.0085 \times 10^{-16} \mathrm{~J}\left(\frac{1 \mathrm{eV}}{1.6022 \times 10^{-19} \mathrm{~J}}\right)=1253.6 \mathrm{eV}
\end{gathered}
$$

(c)

$$
\begin{gathered}
\mathrm{KE}=\frac{1}{2} m_{e} v^{2} \\
\mathrm{KE}_{\mathrm{a}}=\frac{\left(9.10938 \times 10^{-31} \mathrm{~kg}\right)\left(7.992 \times 10^{6} \mathrm{~m} \mathrm{~s}^{-1}\right)^{2}}{2}\left(\frac{1 \mathrm{eV}}{1.6022 \times 10^{-19} \mathrm{~J}}\right)=181.6 \mathrm{eV} \\
\mathrm{KE}_{\mathrm{b}}=\frac{\left(9.10938 \times 10^{-31} \mathrm{~kg}\right)\left(2.046 \times 10^{7} \mathrm{~m} \mathrm{~s}^{-1}\right)^{2}}{2}\left(\frac{1 \mathrm{eV}}{1.6022 \times 10^{-19} \mathrm{~J}}\right)=1190.0 \mathrm{eV} \\
\mathrm{KE}_{\mathrm{c}}=\frac{\left(9.10938 \times 10^{-31} \mathrm{~kg}\right)\left(2.074 \times 10^{7} \mathrm{~m} \mathrm{~s}^{-1}\right)^{2}}{2}\left(\frac{1 \mathrm{eV}}{1.6022 \times 10^{-19} \mathrm{~J}}\right)=1222.8 \mathrm{eV} \\
\mathrm{KE}_{\mathrm{d}}=\frac{\left(9.10938 \times 10^{-31} \mathrm{~kg}\right)\left(2.009 \times 10^{7} \mathrm{~m} \mathrm{~s}^{-1}\right)^{2}}{2}\left(\frac{1 \mathrm{eV}}{1.6022 \times 10^{-19} \mathrm{~J}}\right)=1147.4 \mathrm{eV}
\end{gathered}
$$

(d)

$$
\begin{gathered}
\mathrm{IE}=\mathrm{E}_{\mathrm{X}-\mathrm{ray}}-\mathrm{E}_{\mathrm{k}} \\
\mathrm{IE}_{\mathrm{a}}=1253.6 \mathrm{eV}-181.6 \mathrm{eV}=1072.0 \mathrm{eV} \\
\mathrm{IE}_{\mathrm{b}}=1253.6 \mathrm{eV}-1190.0 \mathrm{eV}=63.6 \mathrm{eV} \\
\mathrm{IE}_{\mathrm{c}}=1253.6 \mathrm{eV}-1222.8 \mathrm{eV}=30.8 \mathrm{eV} \\
\mathrm{IE} \\
\mathrm{~d}
\end{gathered}=1253.6 \mathrm{eV}-1147.4 \mathrm{eV}=106.2 \mathrm{eV} .
$$

(e) The Peak a corresponds to removal of a 1 s electron. Peaks $\mathrm{b}, \mathrm{c}$, and d correspond to removal of a 2 p , a 3 s , and the 2 s electron respectively.


## Physical Constants

Avogadro's number
Bohr radius
Boltzmann's constant
Electronic charge
Faraday constant
Masses of fundamental particles:
Electron
Proton
Neutron
Permittivity of vacuum
Planck's constant
Ratio of proton mass to electron mass
Speed of light in a vacuum
Standard acceleration of terrestrial gravity

$$
\begin{aligned}
& m_{e}=9.10938215 \times 10^{-31} \mathrm{~kg} \\
& m_{P}=1.672621637 \times 10^{-27} \mathrm{~kg} \\
& \mathrm{~m}_{n}=1.674927211 \times 10^{-27} \mathrm{~kg} \\
& \varepsilon_{0}=8.854187817 \times 10^{-12} \mathrm{C}^{-2} \mathrm{~J}^{-1} \mathrm{~m}^{-1} \\
& h=6.62606896 \times 10^{-34} \mathrm{~J} \mathrm{~s} \\
& m_{P} / m_{e}=1836.15267247 \\
& \mathrm{c}=2.99792458 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1} \text { (exactly) } \\
& g=9.80665 \mathrm{~m} \mathrm{~s}^{-2}(\text { exactly })_{R}=8.314472 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \\
&=0.0820574 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}
\end{aligned}
$$

Values are taken from the 2006 CODATA recommended values, as listed by the National Institute of Standards and Technology.

## Conversion factors

| Ångström | $1 \AA=10^{-10} \mathrm{~m}$ |
| :--- | :--- |
| Atomic mass unit | $1 \mathrm{u}=1.660538782 \times 10^{-27} \mathrm{~kg}$ |
|  | $1 \mathrm{u}=1.492417830 \times 10^{-10} \mathrm{~J}=931.494028 \mathrm{MeV}$ (energy equivalent form |
|  | $\left.E=m c^{2}\right)$ |
| Calorie | $1 \mathrm{cal}=4.184 \mathrm{~J}$ (exactly) |
| Electron volt | $1 \mathrm{eV}=1.602177 \times 10^{-19} \mathrm{~J}=96.485335 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| Foot | $1 \mathrm{ft}=12 \mathrm{in}=0.3048 \mathrm{~m}($ exactly) |
| Gallon (U.S.) | 1 gallon $=4$ quarts $=3.785412 \mathrm{~L}$ (exactly) |
|  |  |


| Liter | $1 \mathrm{~L}=10^{-3} \mathrm{~m}^{3}=10^{3} \mathrm{~cm}^{3}$ (exactly) |
| :--- | :--- |
| Liter-atmosphere | $1 \mathrm{~L} \mathrm{~atm}=101.325 \mathrm{~J}$ (exactly) |
| Metric ton | $1 \mathrm{t}=1000 \mathrm{~kg}$ (exactly) |
| Pound | $1 \mathrm{lb}=16 \mathrm{oz}=0.4539237 \mathrm{~kg}$ (exactly) |
| Rydberg | $1 \mathrm{Ry}=2.17987197 \times 10^{-18} \mathrm{~J}=1312.7136 \mathrm{~kJ} \mathrm{~mol}^{-1}=13.60569193 \mathrm{eV}$ |
| Standard atmosphere | $1 \mathrm{~atm}=1.01325 \times 10^{5} \mathrm{~Pa}=1.01325 \times 10^{5} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-2}$ (exactly) |
| Torr | 1 torr $=133.3224 \mathrm{~Pa}$ |









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