2024 SPRING Semester Final Examination
For General Chemistry I

Date: June 12(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
1	/10	**6**	/18	**/100**
2	/14	**7**	/14	
3	/5	**8**	/13	
4	/6	**9**	/10	
5	/10			

** This paper consists of 17 sheets with 9 problems (***page 14 - 16***: Equation, constants & periodic table, ***page 17***: 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: **June 14 (Friday, 12:00 ~ 14:00, 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)**
A	207
B	208
C	Terman Hall
D	409

0 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: ***June 15(Sat.) ~ 16(Sun)***

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. (Total 10 points)

Indicate "O" for correct statements and "X" for incorrect statements.

(1) The standard reduction potential is a ratio scale, like Kelvin. [Hint: Celsius and Fahrenheit are interval scales, but Kelvin is a ratio scale.] (   )

(2) Entropy could be considered to be measured on a ratio scale, in accordance with the third law of thermodynamics. (   )

(3) Given that E_{cell° for $A + B \rightarrow C + D$ is e, E_{cell° for $2A + 2B \rightarrow 2C + 2D$ is also e, because E_{cell° is an extensive property, like ΔG^o. (   )

(4) The steady state in chemical kinetics is an equilibrium state. (   )

(5) The pH value is equal to pKa when [HA] is equal to [A-], especially for weak acids. (   )

(6) All spontaneous processes produce an increase in the entropy of the system. (   )

(7) During phase transitions, the change in enthalpy equals the product of the change in entropy and the absolute temperature. (   )

(8) The equilibrium is reached at the point, where the slope of the Gibbs free energy versus extent of reaction graph is zero. (   )

(9) Fractional distillation can be explained by Henry's law. (   )

(10) Aniline is more basic than cyclohexylamine due to the electron delocalization. (   )

Each 1 point, no partial points

1	**X**		**6**	**X**
2	**O**		**7**	**O**
3	**X**		**8**	**O**
4	**X**		**9**	**X**
5	**O**		**10**	**X**

2. (Total 14 points)

Fill out the blanks

1. The relationship between the standard Gibbs energy change and the equilibrium constant for a reaction is (a). The constant K, is the value of the reaction quotient Q at equilibrium and is call the (b).

2. Osmotic flow can be stopped by applying a pressure, to the more (c) solution. In (d), the direction of flow is reversed by applying a pressure that exceeds the osmotic pressure to the more (c) solution. (e) are certain properties that depend only on the concentration of solution particles in a solution, and not on the identity of the solute.

3. A (f) is a step-by-step description of a chemical reaction consisting of a series of (g). Rate laws are written for the (g) and combined in to a rate law for the overall reaction.

4. The (h) describes an acid as a proton donor and a base as a proton acceptor. The combinations of HA/A- and B/HB+ (HA: an acid, B: a base) are known as (i).

5. Solutions that resist changes in pH upon the addition of small amounts of an acid or base are referred to as (j). Calculating the pH of (j) can be application of the (k) equation.

6. In the (l), E_{cell} for nonstandard conditions is related to E_{Cell}° and the reaction quotient Q. If $E_{cell} > 0$, the cell reaction is (m) in the forward direction for the stated conditions. A (n) consists of two half-cells with identical electrodes but different solution concentrations

Each 1 point, no partial points

a	$\Delta_r G^o = -RT\ln K$		**j**	**buffer solutions**
b	**thermodynamic equilibrium constant (그냥 equilibrium constant도 정답 처리)**		**k**	**Henderson-Hasselbalch**
c	**Concentrated**		**l**	**Nernst equation**
d	**reverse osmosis**		**m**	**spontaneous**
e	**colligative properties**		**n**	**concentration cell**
f	**reaction mechanism**			
g	**elementary processes**			
h	**Brønsted-Lowry theory**			
i	**conjugate acid-base pairs**			

3. (Total 5 points)

One proposed mechanism for the reaction between 2-chloroethnaol, CH_2ClCH_2OH, and hydroxide ions in aqueous solution, is as follows:

$$CH_2ClCH_2OH + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2ClCH_2O^- + H_2O$$

$$CH_2ClCH_2O^- \xrightarrow{k_2} (CH_2CH_2)O + Cl^-$$

Use the steady-state approximation to determine the rate of formation for the product, $(CH_2CH_2)O$.

Using the steady-state approximation, while its concentration is not known during the reaction, the rate of change of its concentration is zero. Therefore,

$$\frac{d[CH_2ClCH_2O^-]}{dt} = k_1[CH_2ClCH_2OH][OH^-] - k_{-1}[CH_2ClCH_2O^-][H_2O] - k_2[CH_2ClCH_2O^-] = 0$$

(2 points)

Rearranging the above expression to solve for $[CH_2ClCH_2O^-]$ gives the following expression

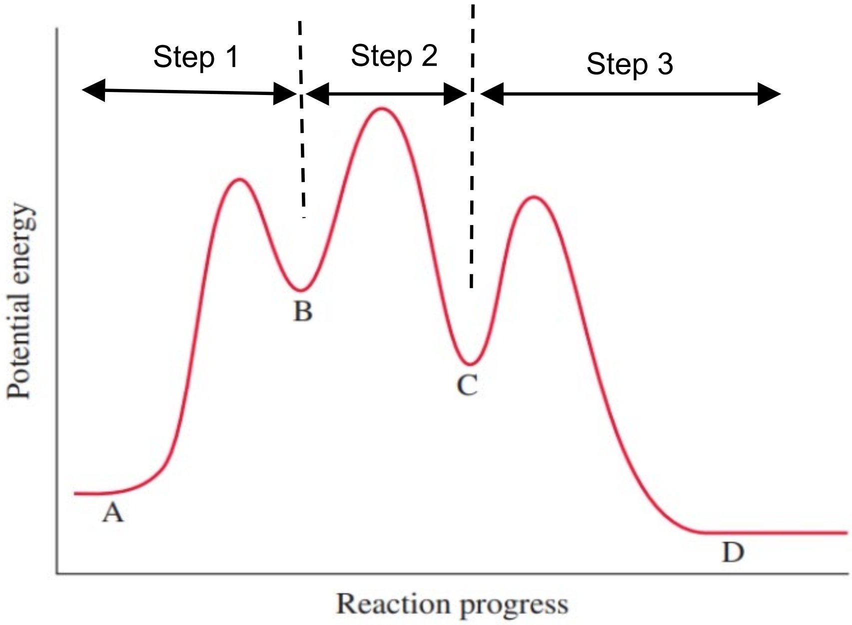
$$\left[CH_2ClCH_2O^-\right] = \frac{k_1[CH_2ClCH_2OH][OH^-]}{k_{-1}[H_2O] + k_2} \quad \text{(1point)}$$

The rate of formation of $(CH_2CH_2)O$ is therefore

$$\frac{d[(CH_2CH_2)O]}{dt} = k_2\left[CH_2ClCH_2O^-\right] = \frac{k_2 k_1[CH_2ClCH_2OH][OH^-]}{k_{-1}[H_2O] + k_2} \quad \text{(2 points)}$$

4. (Total 6 points)

By inspection of the reaction profile for the reaction A to D given below, answer the following questions. (6 points, each question is one point)



(a) How many intermediates are there in the reaction?

(b) How many transition states are there?

(c) Which step has the largest rate constant?

(d) Which step has the smallest rate constant?

(e) Is the first step of the reaction exothermic or endothermic?

(f) Is the overall reaction exothermic or endothermic?

Each 1 point

(a) There are two intermediates (B and C).

(b) There are three transition states (peaks/maxima) in the energy diagram.

(c) The fastest step has the smallest Ea, hence, step 3 is the fastest step in the reaction.

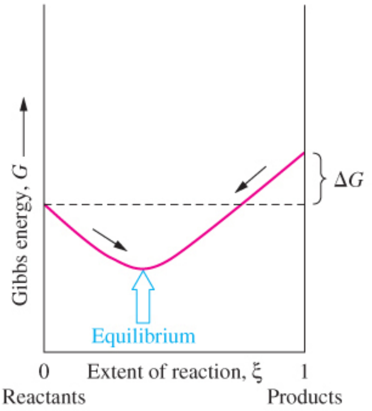
(d) Reactant A (step 1) has the highest Ea, and therefore the slowest smallest constant

(e) Endothermic; energy is needed to go from A to B.

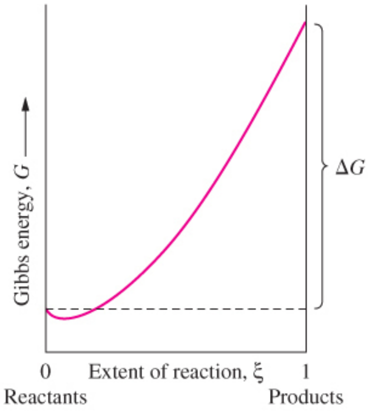
(f) Exothermic; energy is released moving from A to D.

5. (Total 10 points)

The below contains Gibbs energy plotted against the extent of the reaction for a reaction $aA + bB \rightarrow cC + dD$. For $\xi = 1$ mol, the system contains stoichiometric amounts of products (c mol C and d mol D) at a total pressure P. $\Delta G = -1 \text{ mol} \times RT \ln K + \text{constant}$. Please answer the questions depending on estimated K values.



a



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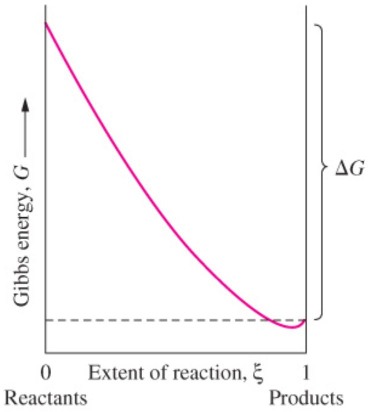


c

(a) (3pts) Explain what the positive or negative slope of the red graph means. Which one has the highest and the lowest K value?

(b) (4pts with 2pts each) For reaction $2Cl_2O(g) \rightarrow 2Cl_2(g) + O_2(g)$ $\Delta_rH = -161$ kJ/mol, is the entropy change positive or negative? Explain. (3pts → **2pts**) Is the reaction spontaneous at high or low temperatures? Explain. (3 pts → **2pts**)

(c) (3pts) Which of the following graphs of Gibbs energy versus the extent of reaction represents an equilibrium constant close to 1?

Answer

(a) (3 pts) The positive slope means ΔG is positive and the negative one means ΔG is negative. At c, $K >> 1$ (ΔG has a large negative value), at b, $K << 1$ (ΔG has a large positive value), at a, $K \approx 1$

(b) Spontaneous in both cases due to the negative enthalpy and entropy: To answer this question, we must first determine whether the entropy change for the given reaction is positive or negative. The reaction produces three moles of gas from two moles; therefore, the entropy change for the reaction is positive. The Gibbs energy of a reaction is a function of enthalpy, entropy, and temperature ($\Delta_rG = \Delta_rH - T\Delta_rS$). Since $\Delta_rH < 0$ and $\Delta_rS > 0$, this reaction will be spontaneous at any temperature.

(c) Recall from (b) that, when $K = 1$. Therefore, we are looking for the graph with the smallest change in Gibbs energy between the products and the reactants. The correct answer is graph (a).

6. (Total 18 points)

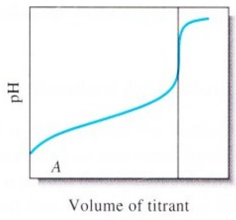
Use the table to answer the following questions.

Acid	**K_a**
HNO_2	7.1×10^{-4}
CH_3COOH (HOAc)	1.75×10^{-5}
NH_4^+	5.70×10^{-10}
H_3PO_4	7.11×10^{-3} ; 6.32×10^{-8} ; 4.5×10^{-13}
ethylene diammonia ($^+H_3NCH_2CH_2NH_3^+$)	1.42×10^{-7}; 1.18×10^{-10}
salicylic acid ($C_6H_4(OH)COOH$)	1.06×10^{-3}
lactic acid	1.38×10^{-4}
Bromocresol green	2.19×10^{-5}
Bromothymol blue	7.94×10^{-8}
phenolphthalein	4.0×10^{-10}

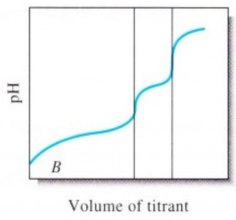
(a). (5 pts) Determine whether the aqueous solution of each of the following compounds is acidic, basic, or neutral.

(1) $NaNO_2$ (2) Na_2HPO_4 (3) NaH_2PO_4 (4) Na_3PO_4 (5) NH_4OAc

(b) (2 pts) Which titration curve would you expect when you titrate the aqueous solution of ethylene diammonia $H_2NCH_2CH_2NH_2$ (titrant) with an acid with known concentration (acid titrant)?



A



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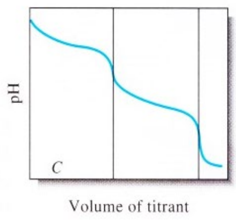
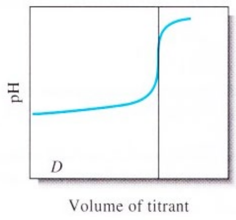


C



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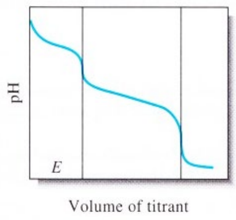
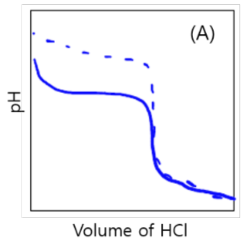
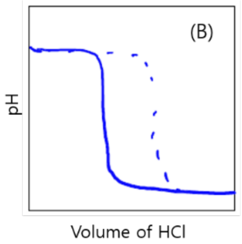
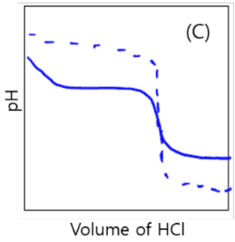


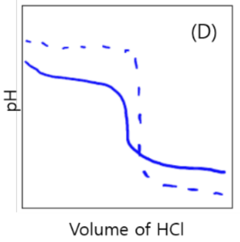
E

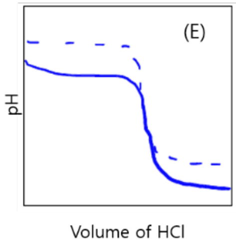
(c). (2 pts)Which figure describes curves for the titration of 0.10 M NH_3 (solid curve) and 0.10 M NaOH (dashed curve) with 0.10 M HCl correctly?











(d). (3 pts) Which of the following titration will have the largest error (in the volume of titrant)?

(1) Titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH using phenolphthalein

(2) Titration of 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH using bromothymol blue

(3) Titration of 50.00 mL of 0.0100M H_2SO_4 with 0.0100M NaOH using bromocresol green

(4) Titration of 50.00 mL of 0.0100M lactic acid with 0.0100M NaOH using bromothymol blue

(5) Titration of 50.00 mL of 0.0100M NaH_2PO_4 with 0.0100M NaOH using bromocresol green

(e). (3 pts) Which of the following is correct?

(1) The pH of a buffer solution never changes regardless of addition of strong acid or base.

(2) The pH of a buffer solution is constant regardless of the concentration of buffer components (HA and NaA).

(3) Before equivalence points, a curve for the titration of acetic acid with NaOH is almost constant regardless of the concentration of acetic acid.

(4) Buffer capacity is a function of pKa.

(5) Strong base and its conjugate acid can form a buffer solution.

(f). (3 pts) Which of the following is incorrect?

(1) Indicators used for neutralization titration themselves are either acids or bases.

(2) Species whose acid forms and conjugated base forms have distinctively different colors can be utilized as indicators.

(3) Indicators' pH transition ranges depend on titrant's pKa's.

(4) When a weak acid is titrated with a strong base, indicator with its pKa > 7 should be used.

(5) When a strong acid is titrated with a strong base, the choice of indicator should depend on the concentration of analyte.

\

(a)

(1) $NO_2^- + H_2O \rightleftarrows HNO_2 + OH^-$; thus, the solution will be basic.

(2) $HPO_4^{2-} + H_2O \rightleftarrows H_3O^+ + PO_4^{3-} \quad K_3 = 4.5 \times 10^{-13}$

$$HPO_4^{2-} + H_2O \rightleftarrows OH^- + H_2PO_4^- \; K_b = \frac{1.00 \times 10^{-14}}{6.32 \times 10^{-8}} = 1.58 \times 10^{-7}$$

The second reaction is more dominant than the first one ($K_3 < K_b$); thus, the solution will be basic.

(3) $H_2PO_4^- + H_2O \rightleftarrows H_3O^+ + HPO_4^- K_2 = 6.32 \times 10^{-8}$

$$H_2PO_4^- + H_2O \rightleftarrows OH^- + H_3PO_4 K_b = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$$

Here $K_2 > K_b$, so the first reaction is more dominant; thus, the solution will be acidic.

(4) $PO_4^{3-} + H_2O \rightleftarrows HPO_4^{2-} + OH^- K_b = \frac{1.00\times10^{-14}}{4.5\times10^{-13}} = 2.2 \times 10^{-2}$; thus, the solution will be basic.

(5) $NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+ \qquad K_{NH4+} = 5.70 \times 10^{-10}$

$OAc^- + H_2O \rightleftarrows HOAc + OH^- \qquad K_{OAc-} = K_w/K_{HOAc} = 5.71 \times 10^{-10}$

$K_{NH4+} \sim K_{OAc-}$ Thus, the solution will be roughly neutral.

(b) The answer is C. Because of the following two reactions, the ethylene diammonia aquestion solution is basic and there are two equivalence points. Each reaction takes the same amount of titrant. Thus, D is incorrect.

$H_2NCH_2CH_2NH_2 + H_2O \rightleftarrows H_2NCH_2CH_2NH_3^+ + OH^- \qquad K_{b1} = Kw/K_{a2} = 8.5 \times 10^{-5}$

$H_2NCH_2CH_2NH_3^+ + H_2O \rightleftarrows {}^+H_3NCH_2CH_2NH_3^+ + OH^- \quad K_{b2} = Kw/K_{a1} = 7.0 \times 10^{-8}$

(c) The answer is A.

Initial point before titration: pH of NaOH solution > pH of NH_3

Before equivalence point after beginning of the titration: There is NH_3 alone in the beginning and thus no buffer capacity will be observed. However, once the conjugated acid is formed, it becomes a buffer. Therefore, there will be a steep change in pH in the early phase while pH plateau will be observed afterwards.

At equivalence point: the same mole of HCl will be required to titrate either NaOH or NH_3, while the latter one will have a smaller change in pH near the equivalence point.

After the equivalence point: Adding more HCl is just like adding HCl into a neutral solution. Thus, the same change in pH for both solutions will be observed.

(d) The answer is 5.

The Ka's of indicators show that phenolphthalein, bromothymol blue, and bromocresol green are basic, neutral, and acidic indicators, respectively.

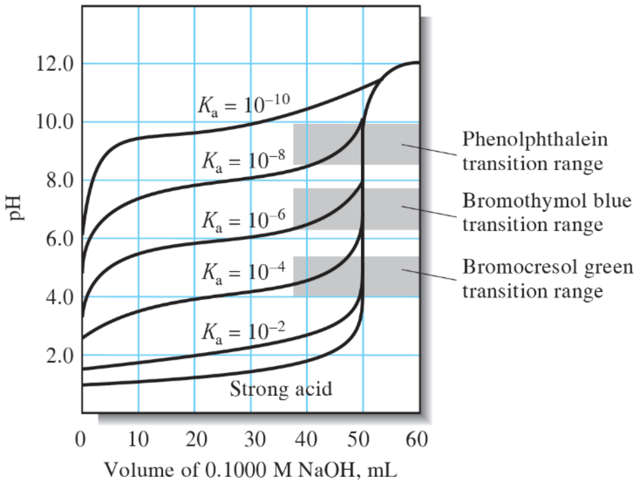
1 A strong acid and base reaction with a neutral equivalence point and large pH change => any indicator can be used.

2 A strong acid and base reaction with a neutral equivalence point but a small pH change due to dilute solutions => neutral indicator is ideal.

3 H_2SO_4 has an extremely large Ka_1 and thus both protons are dissociated at almost any pH. Only one neutral equivalence point (requiring double volume of basic solution compared to equivalent concentration HCl) with large pH change. => any indicator can be used.

4 Weak acid ($Ka \sim 10^{-4}$) + strong base reaction; thus slightly basic equivalence point => neutral and basic indicators can be used (see below)

5 Very weak acid $H_2PO_4^-$ ($Ka \sim 10^{-8}$) + strong base reaction; basic equivalence point => acidic indicator cannot be used.



(e) The answer is 3.

(f) The answer is 3.

7. (Total 14 points)

Currently, CO_2 is being studied as a source of carbon atoms for synthesizing organic compounds. One possible reaction involves the conversion of CO_2 to methanol, CH_3OH.

$$CO_2(g) + 3H_2(g) \longrightarrow CH_3OH(g) + H_2O(g)$$

	$CO_2(g)$	$H_2(g)$	$CH_3OH(g)$	$H_2O(g)$
$\Delta_r H^o$ (kJ/mol)	-393.5	0	-200.7	-241.8
$\Delta_r S^o$ (J/mol K)	213.7	130.7	239.8	188.8

(a) (6 pts) Using the data provided in the table, determine the reaction enthalpy, entropy, and Gibbs free energy at 298K.

(b) (2 pt) At 298K, does this reaction proceed to any significant extent?

(c) (3 pts) Explain how the production of methanol can be favored by either raising or lowering the temperature from 298K.

(d) (3 pts) Calculate the equilibrium constant at 500K.

(a) We determine the values of $\Delta_r H°$ and $\Delta_r S°$ from the data in Appendix D, and then the value of $\Delta_r G°$ at $25\ °C = 298\ K$.

$$\Delta_r H° = \Delta_f H°[CH_3OH(g)] + \Delta_f H°[H_2O(g)] - \Delta_f H°[CO_2(g)] - 3\,\Delta_f H°[H_2(g)]$$

$$= -200.7\,kJ/mol + (-241.8\,kJ/mol) - (-393.5\,kJ/mol) - 3(0.00\,kJ/mol) = -49.0\,kJ/mol$$

$$\Delta_r S° = S°[CH_3OH(g)] + S°[H_2O(g)] - S°[CO_2(g)] - 3\,S°[H_2(g)]$$

$$= (239.8 + 188.8 - 213.7 - 3\times130.7)\,J\ mol^{-1}K^{-1} = -177.2\,J\ mol^{-1}K^{-1}$$

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -49.0\,kJ/mol - 298\,K\left(-0.1772\,kJ\ mol^{-1}K^{-1}\right) = +3.81\,kJ/mol$$

2 pts each

(b) Because the value of $\Delta_r G°$ is positive, this reaction does not proceed in the forward direction at 25°C.

(c) Because the value of $\Delta_r H°$ is negative and that of $\Delta_r S°$ is negative, the reaction is *non-spontaneous* at high temperatures, if reactants and products are *in their standard states*. The reaction will proceed slightly in the forward direction, however, to produce an equilibrium mixture with small quantities of $CH_3OH(g)$ and $H_2O(g)$. Also, because the forward reaction is exothermic, this reaction is favored by lowering the temperature. That is, the value of K increases with decreasing temperature.

(d)

$$\Delta_r G^o_{500K} = \Delta_r H° - T\Delta_r S° = -49.0\,kJ/mol - 500.K\left(-0.1772\,kJ\ mol^{-1}\ K^{-1}\right) = 39.6\,kJ/mol$$

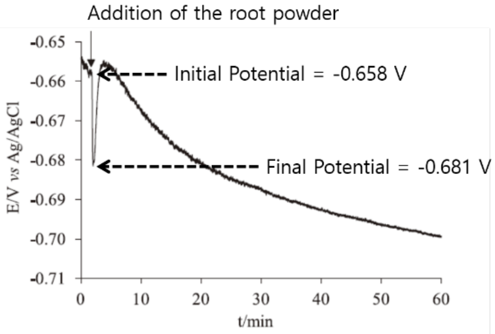
$$= 39.6\times10^3\ J/mol = -RT\ln K_p$$

$$\ln K = \frac{-\Delta_r G°}{RT} = \frac{-39.6\times10^3\ J/mol}{8.3145\,J\ mol^{-1}K^{-1}\times 500.\ K} = -9.53; \quad K = e^{-9.53} = 7.3\times10^{-5}$$

8. (Total 13 points)

Industrial development has resulted in the release of toxic compounds such as heavy metals into the environment. One of novel removal strategies is biosorption, which refers to the adsorption of metal ions on dead biomass such as algae, crop residues, and fungi. This metal uptake by nonliving materials is an emerging low-cost, effective, and environmentally friendly technology.

The roots of *Eichhornia crassipes* were collected from a greenhouse, washed with deionized water, dried at oven and ground to a fine powder. To examine the biosorption capability of this material, $Cd(NO_3)_2$ in 0.100 M $NaClO_4$ solution was prepared and its open circuit potential was measured at -0.658 V with respect to an Ag|AgCl(NaCl 3 M) reference electrode. Upon addition of the root powder to the Cd^{2+} solution, the potential drops down to -0.681 V.



(a) (3 pts) Which of the following is a correct scheme for this potential measurement?

1. AgCl | Ag | NaCl (3M) || Cd(II) | Cd
2. AgCl | Ag | NaCl (3M)|| Cd | Cd (II)
3. Cd(II) | Cd || AgCl | NaCl (3M) | Ag
4. Cd | Cd (II) || AgCl | NaCl (3M) | Ag
5. Ag | AgCl | NaCl (3M) || Cd(II) | Cd

(b) (5 pts)With respect to SHE, $E^{\circ}_{Ag(I)/Ag^{+}}$ is + 0.799 V, and K_{sp} for AgCl(s) is $K_{sp} = [Ag^{+}][Cl^{-}] = 1.82 \times 10^{-10}$. Then, what is the electric potential E_{ref} of the Ag|AgCl (NaCl 3M) reference electrode with respect to SHE?

(c) (3 pts)The standard reduction potential of Cd^{2+} is -0.403 V with respect to SHE. What was the initial concentration of $Cd(NO_3)_2$?

(d). (2 pts) What percentage of Cd^{2+} was adsorbed by the root powder?

(a) The answer is 5.

(b) The answer is +0.194 V.

$$Ag^+(aq) + e^- \rightarrow Ag(s) \quad \Delta G_1^0 = -zFE^\circ = -1 \cdot F \cdot (0.799\ V)$$

$$\mathrm{AgCl(s)} \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad \Delta G_2^0 = -RTln\ K = -RT\ln(1.82 \times 10^{-10})$$

$$\mathrm{AgCl}(s) + e^- \rightarrow \mathrm{Ag}(s) + \mathrm{Cl}^-(aq) \quad \Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

$$= -1 \cdot F \cdot (0.799\ \mathrm{V}) - RT\ln(1.82 \times 10^{-10})$$

$$\Delta G_3 = \Delta G_3^0 + RTlnQ = -zFE_{ref}$$

$$Q = [\mathrm{Cl}^-(aq)] = 3\ \mathrm{M}$$

$$= -1 \cdot F \cdot (0.799\ \mathrm{V}) - RTln(1.82 \times 10^{-10}) + RTln([Cl^-(aq)]) = -1 \cdot F \cdot E_{ref}$$

Divide both sides by -F, and we get:

$$E_{ref} = (0.799\ \mathrm{V}) + \left(\frac{RT}{F}\right)\ln(1.82 \times 10^{-10}) - \left(\frac{RT}{F}\right)ln(3\ \mathrm{M}) = 0.194\ \mathrm{V}$$

(c) The answer is 8.7×10^{-3}M.

$E_{cell} = E^0(\mathrm{Cd(II)|Cd}) + (0.0257/2)\ln[\mathrm{Cd(II)}] - E_{ref}$

-0.658 V = -0.403 V + (0.0257/2)ln[Cd(II)] – 0.194 V

$[\mathrm{Cd(II)}]_{initial} = 8.7\times 10^{-3}$M

(d) The answer is 83 %.

Using the above eqn, $[\mathrm{Cd(II)}]_{final} = 1.5\times 10^{-3}$ M

9. (Total 10 points)

For the voltaic cell,

$$\mathrm{Fe(s)\mid Fe^{2+}\,(aq)\parallel Fe^{3+}\,(aq),\ Fe^{2+}\,(aq)\mid Pt(s)}$$

(a) (2 pts) Derive a balanced equation for the reaction occurring in the cell

(b) (2 pts) If $E^{\circ}_{\text{cell}} = 1.21$ V, calculate $\Delta_r G^{\circ}$ and the equilibrium constant for the reaction.

(c) (4 pts) Determine the potential for the cell:

$$\mathrm{Fe(s)\mid Fe^{2+}\,(aq,\ 1.0\times10^{-3}\ M)\parallel Fe^{3+}\,(aq,\ 1.0\times10^{-3}\ M),\ Fe^{2+}\,(aq,\ 0.10\ M)\mid Pt(s)}$$

(d) (2 pts) In light of (b) and (c), what is the likelihood of being able to observe the disproportionation of Fe^{2+} into Fe^{3+} and Fe under standard conditions?

(a) We proceed by first deriving a balanced equation for the reaction occurring in the cell:

Oxidation: $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-}$

Reduction: $\mathrm{\{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)\} \times 2}$

Net: $\mathrm{Fe(s) + 2\,Fe^{3+}(aq) \rightarrow 3\,Fe^{2+}(aq)}$

(b) $\Delta_r G^{\circ}$ and the equilibrium constant K can be calculated using

$$\Delta_r G^{\circ} = -zFE^{\circ}_{\text{cell}} = -RT\ln K:$$

$$\Delta_r G^{\circ} = -zFE^{\circ}_{\text{cell}} = -2\times 96485\ \mathrm{C\ mol^{-1}} \times 1.21\ \mathrm{V} = -233.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r G^{\circ} = -RT\ln K = -8.314\ \mathrm{J\ K^{-1}mol^{-1}} \times 298.15\ \mathrm{K} \times \ln K = -233.5\times 1000\ \mathrm{J\ mol^{-1}}$$

$$\ln K = 94.2 \Rightarrow K = e^{94.2} = 8.1\times 10^{40}$$

(c) Before calculating voltage using the Nernst equation, we need to re-write the net reaction to take into account concentration gradient for Fe^{2+}(aq):

Oxidation: $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq, 1.0\times10^{-3}\ M) + 2\,e^-}$

Reduction: $\mathrm{\{Fe^{3+}(aq, 1.0\times10^{-3}\ M) + e^- \rightarrow Fe^{2+}(aq,\ 0.10\ M)\} \times 2}$

Net: $\mathrm{Fe(s) + 2\,Fe^{3+}(aq,\ 1.0\times10^{-3}\ M) \rightarrow Fe^{2+}(aq,\ 1.0\times10^{-3}\ M) + 2\,Fe^{2+}(aq,\ 0.10\ M)}$

Therefore,

$$Q = \frac{1.0\times10^{-3}\times(0.10)^2}{(1.0\times10^{-3})^2} = 10$$

Now, we can apply the Nerst equation to calculate the voltage:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257\ \mathrm{V}}{z}\ln Q = 1.21\ \mathrm{V} - \frac{0.0257}{2}\ln 10 = 1.18\ \mathrm{V}$$

(d) From parts (b) and (c) we can conclude that the reaction between Fe(s) and Fe^{3+}(aq) is spontaneous. The reverse reaction (i.e. disproportionation of Fe^{2+}(aq)) must therefore be nonspontaneous.

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23}$ mol^{-1}
Bohr radius	$a_0 = 0.52917720859$ Å $= 5.2917720859\text{x}10^{-11}$ m
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23}$ J K^{-1}
Electronic charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96485.3399$ C mol^{-1}
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31}$ kg
Proton	$m_P = 1.672621637 \times 10^{-27}$ kg
Neutron	$\mathrm{m}_n = 1.674927211 \times 10^{-27}$ kg
Permittivity of vacuum	$\varepsilon_o = 8.854187817 \times 10^{-12}$ C^{-2} J^{-1} m^{-1}
Planck's constant	$h = 6.62606896 \times 10^{-34}$ J s
Ratio of proton mass to electron mass	$m_P / m_e = 1836.15267247$
Speed of light in a vacuum	c = 2.99792458×10^8 m s^{-1} (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665$ m s^{-2} (exactly)
Universal gas constant	$R = 8.314472$ J mol^{-1} K^{-1} $= 0.0820574$ L atm mol^{-1} K^{-1}

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

Conversion factors

Ångström	1 Å= 10^{-10} m
Atomic mass unit	1 u = $1.660538782 \times 10^{-27}$ kg 1 u = $1.492417830 \times 10^{-10}$ J = 931.494028 MeV (energy equivalent form $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = 1.602177×10^{-19} J = 96.485335 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U. S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	1 L = 10^{-3} m^3 = 10^3 cm^3 (exactly)

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

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS
IUPAC RECOMMENDATION
(1985)

GROUP NUMBERS
CHEMICAL ABSTRACT SERVICE
(1986)

13 IIIA
ATOMIC NUMBER — 5 10.811 — RELATIVE ATOMIC MASS (1)
SYMBOL — B
BORON — ELEMENT NAME

PERIOD \ GROUP	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** **Lanthanide**	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** **Actinide**	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

LANTHANIDE

6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

Claim Form for General Chemistry Examination

Page (/)

Class:__________, Professor Name:__________, I.D.# :____________, Name:____________________

If you have any claims on the marked paper, please write down them on this form and *submit this with your paper in the assigned place.* (And this form should be attached *on the top of the marked paper with a stapler.*) Please, *copy this sheet if you need more bef*

By Student		By TA	
Question #	Claims	Accepted? Yes(√) or No(√)	
		Yes: ☐	No: ☐
		Pts (+/-)	Reasons

2024 SPRING Semester Mid-term Examination
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
1	/15	**6**	/8	**/100**
2	/8	**7**	/10	
3	/8	**8**	/16	
4	/10	**9**	/15	
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)**
A	301
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.

$$S(s) + OCl^{-}(aq) \longrightarrow SO_3^{2-}(aq) + Cl^{-}(aq)$$

(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 (K_3PO_4) was added to 15.0 mL of 0.050 M silver nitrate ($AgNO_3$) 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) 1-propanol.

(a)

Step 1: Write the two skeleton half-equations.

$$S(s) \rightarrow SO_3^{2-}(aq) \quad \text{and} \quad OCl^{-}(aq) \rightarrow Cl^{-}(aq)$$

Step 2: Balance each skeleton half-equation for O (with H_2O) and for H atoms (with H^+).

$$3\ H_2O(l) + S(s) \rightarrow SO_3^{2-}(aq) + 6\ H^+$$

$$OCl^{-}(aq) + 2\ H^+ \rightarrow Cl^{-}(aq) + H_2O(l)$$

Step 3: Balance electric charge by adding electrons.

$$3\ H_2O(l) + S(s) \rightarrow SO_3^{2-}(aq) + 6\ H^+(aq) + 4\ e^-$$

$$OCl^{-}(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow Cl^{-}(aq) + H_2O(l)$$

Step 4: Change from an acidic medium to a basic one by adding OH^- to eliminate H^+.

$$3H_2O(l) + S(s) + 6\ OH^-(aq) \rightarrow SO_3^{2-}(aq) + 6\ H^+(aq) + 6\ OH^-(aq) + 4\ e^-$$

$$OCl^{-}(aq) + 2\ H^+(aq) + 2\ OH^-(aq) + 2\ e^- \rightarrow Cl^{-}(aq) + H_2O(l) + 2\ OH^-(aq)$$

Step 5: Simplify by removing the items present on both sides of each half-equation, and combine the half-equations to obtain the net redox equation.

$$\textit{Oxidation}: S(s) + 6\ OH^-(aq) \rightarrow SO_3^{2-}(aq) + 3\ H_2O(l) + 4\ e^-$$

$$\underline{\textit{Reduction}: \{\mathrm{OCl^-(aq) + H_2O(l) + 2\ e^- \rightarrow Cl^-(aq) + 2\ OH^-(aq)}\} \times 2}$$

$$\textit{Overall}: \mathrm{S(s) + 6\ OH^-(aq) + 2\ OCl^-(aq) + 2H_2O(l) \rightarrow SO_3^{2-}(aq) + 3\ H_2O(l) + 2\ Cl^-(aq) + 4\ OH^-}$$

Simplify by removing the species present on both sides.

Net ionic equation: $\mathrm{S(s) + 2\ OH^-(aq) + 2\ OCl^-(aq) \rightarrow SO_3^{2-}(aq) + H_2O(l) + 2\ Cl^-(aq)}$

(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)
$K_3PO_4(aq) + 3AgNO_3(aq) \longrightarrow Ag_3PO_4(s) + 3KNO_3(aq)$
K_3PO_4 70.5 mg = 0.0705/212 = 0.333 mmol.
$AgNO_3$ = 0.050 M x 15.0 mL = 0.75 mmol.
K_3PO_4 and $AgNO_3$ react in a 1:3 ratio. Limiting reactant = $AgNO_3$.
$AgNO_3$ and Ag_3PO_4 have a 3:1 relationship.
Precipitated Ag_3PO_4 occurs at 1/3 (mol) of the occurrence of $AgNO_3$
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)

CCl_4, an important commercial solvent, is prepared by the reaction of $Cl_2(g)$ with a carbon compound.

Determine $\Delta_r H°$ for the reaction

$$CS_2(l) + 3Cl_2(g) \rightarrow CCl_4(l) + S_2Cl_2(l) \quad \Delta_r H° = ?$$

Use appropriate data from the following listing.

$$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) \quad \Delta_r H_1° = -1077 \text{ kJ mol}^{-1}$$

$$2S(s) + Cl_2(g) \rightarrow S_2Cl_2(g) \quad \Delta_r H_2° = -58.2 \text{ kJ mol}^{-1}$$

$$C(s) + 2Cl_2(g) \rightarrow CCl_4(l) \quad \Delta_r H_3° = -135.4 \text{ kJ mol}^{-1}$$

$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_r H_4° = -296.8 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H_5° = -393.5 \text{ kJ mol}^{-1}$$

First, we can see that we are able to get the necessary reactants by combining first three reactions.
$CS_2 + 3O_2 + C + 3Cl_2 + 2S \rightarrow CO_2 + CCl_4 + S_2Cl_2 + 2SO_2$ (3 points)
However, this reaction has chemical species that need to be eliminated: O_2, C, 2S, CO_2, and SO_2.
Using the last two reactions, all of these chemical species could be eliminated.
Therefore,

$$\Delta_r H° = \Delta_r H_1° + \Delta_r H_2° + \Delta_r H_3° - 2 \times \Delta_r H_4° - \Delta_r H_5°$$

$= -284 \text{ kJ mol}^{-1}$ *(5 ponts)*

3. (8 points)

Consider a scenario where an electron is removed from a fluorine molecule, resulting in the formation of an F_2^+ molecular ion.

(a) (2 points) Provide the molecular electron configurations for both F_2 and F_2^+.

(b) (2 points) Determine and state the bond order for each species, F_2 and F_2^+.

(c) (2 points) Based on the electron configurations, identify which species (F_2 or F_2^+) is expected to be paramagnetic.

(d) (2 points) Using your understanding of molecular structure and bonding, predict which species, F_2 or F_2^+, possesses higher bond dissociation energy.

Answer

(a) (2 pts)

F_2 is a homonuclear diatomic molecule, which has 18 electrons of which 14 are valence electrons. The F_2^+ ion has lost a valence electron and so has 13. Based on the correlation diagram for F_2, the energetic order can be obtained like the following.

F_2 $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$

F_2^+ $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$

(b) (2 pts) The F_2 molecule has two more bonding than antibonding electrons. Its order is 1; F_2^+ ion has three more bonding than antibonding electrons. Its bonding order is 3/2.

(c) (2 pts) The F_2 molecule has zero unpaired electrons. Accordingly, F_2 is diamagnetic. The F_2^+ ion has an odd number of electrons. Because at least one electron (a π^*_{2p} electron) is unpaired. So, F_2^+ ion is paramagnetic.

(d) (2 pts) The F_2^+ ion has a larger bond order and therefore requires more energy to dissociate than F_2^+ ion's case.

4. (10 points)

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

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

Where k_B is Boltzmann constant, T is temperature, and v is the speed.

(a) (4 points) Show that the root-mean-square speed (u_{rms}) is larger than the most probable speed (u_m).

(b) (3 points) Calculate the ratio of rms speed of H_2 to that of N_2 at room temperature (v_{rms}, H_2/v_{rms}, N_2).

(c) (3 points) Calculate the ratio of rms speed of H_2 at 273 °C to that of H_2 at 0°C (v_{rms} at 273 °C/ v_{rm} at $_s$ 0°C).

Answer: (a)

Most probable speed:

$$v_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}} \qquad \left[\frac{df(v)}{dv} = 0\right]_{v=v_{mp}}$$

Mean square speed:

$$\overline{v^2} = \int_0^\infty v^2 f(v)dv = \frac{3k_BT}{m} = \frac{3RT}{M}$$

Root-mean-square speed:

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}$$

So root-mean-square speed is larger than the most probable speed

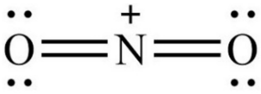
(b) v_{rms}, H_2/v_{rms}, $N_2 = (M_{N2}/ M_{H2})^{1/2} = 14^{1/2}$

(c) v_{rms} at 273 °C/ v_{rm} at $_s$ °C = $(273+273\ K / 273K)^{1/2} = 2^{1/2}$

5. (10 points)

Answer the following questions.

(a) (2 points) Draw the most accepted Lewis (dot) structure for NO_2^+, predict its molecular shape according to the VSEPR model, and assign the appropriate hybridization for the central N atom.

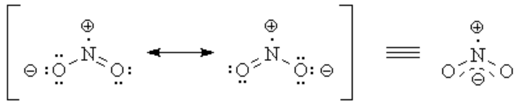


SN=2; linear → *sp*

Structure: +1

Hybridization: +1

(b) (3 points) Draw the most accepted Lewis (dot) structure for NO_2, predict its molecular shape according to the VSEPR model, and assign the appropriate hybridization for the central N atom.



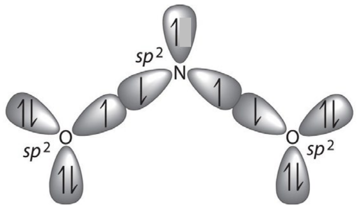
SN=3; bent → *sp^2*

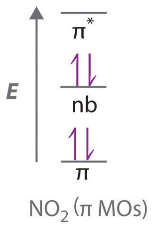
Structure: +1

Hybridization: +1

Resonance: +1

(c) (2 points) You have studied the delocalized π-bonding molecular orbitals for ozone in class. Likewise, draw an energy-level diagram of the π-bonding molecular orbitals, with electrons allocated, <u>based on the Lewis structure for NO_2 proposed in (b)</u>.



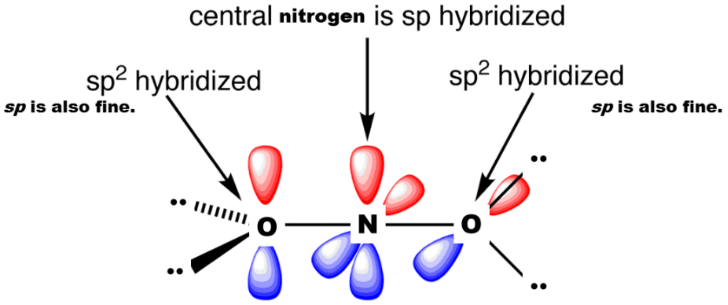


Energy diagram: +1

Electrons: +1

<u>* It is NOT needed to draw something like the left one.</u>

(d) (3 points) Draw an energy-level diagram of the π-bonding molecular orbitals, with electrons allocated, based on the Lewis structure for NO_2^+ given in (a). OR describe the bond (σ and π) characters/geometries with the hybridization concept.



the π bonds formed as a result of the overlap of the p orbitals must be at right angles to each other

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)

$$E_n = \frac{n^2h^2}{8mL^2}$$

$$E_2 - E_1 = (2^2 - 1^2)\cdot\frac{h^2}{8mL^2} = \frac{3h^2}{8mL^2} = \frac{3\times(6.626\times10^{-34} J\, s^{-1})^2}{8\times(9.109\times10^{-31}\,kg)\times(1.2\times10^{-9}\,m)^2}$$

$$= 1.3\times10^{-19} J = h\frac{c}{\lambda} \ldots + 1\text{ pt}$$

$$\therefore \lambda = \frac{hc}{E_2 - E_1} = \frac{(6.626\times10^{-34} J\, s^{-1})\times(2.998\times10^{8}\,m\,s^{-1})}{1.3\times10^{-19} J} = 1520\,nm \ldots + 2\,pt$$

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

(b)

$$E_3 - E_1 = (3^2 - 1^2)\cdot\frac{h^2}{8mL^2} = \frac{8h^2}{8mL^2} = \frac{8\times(6.626\times10^{-34} J\, s^{-1})^2}{8\times(9.109\times10^{-31}\,kg)\times(1.2\times10^{-9}\,m)^2}$$

$$= 3.3\times10^{-19} J = h\frac{c}{\lambda} \ldots + 1\text{ pt}$$

$$\lambda = \frac{hc}{E_2 - E_1} = \frac{(6.626\times10^{-34} J\, s^{-1})\times(2.998\times10^{8}\,m\,s^{-1})}{3.3\times10^{-19} J} = 600\,nm \ldots + 2\text{ pt}$$

It is within the 400 nm – 700 nm region, so it DOES result in the visible spectrum.

(c)

For any transition from n_i to n_f where i>f,

$$\lambda = \frac{hc}{\Delta E} = hc\times\frac{8mL^2}{(n_i^2 - n_f^2)h^2} = \frac{8mcL^2}{(n_i^2 - n_f^2)h}$$

$$= \frac{8\times(9.109\times10^{-31}\,kg)\times(2.998\times10^{8}\,m\,s^{-1})\times(1.2\times10^{-9}\,m)^2}{(n_i^2 - n_f^2)\times(6.626\times10^{-34} J\, s^{-1})} = \frac{475\,nm}{n_i^2 - n_f^2}$$

In order to fall in the visible region:

$$400\,nm < \frac{475\,nm}{n_i^2 - n_f^2} < 700\,nm \ldots + 2\text{ pt}$$

$$6.78 < n_i^2 - n_f^2 < 11.9$$

There are four transitions satisfying this condition: 3 to 1, 4 to 3, 5 to 4, and 6 to 5. …+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 π-bonding molecular orbital that extends over two adjacent carbon atoms in ethene. The electron can move *freely* between the two C atoms. The internuclear C=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.

\>>

$$E_n = \frac{n^2h^2}{8mL^2}$$

$$E_2 - E_1 = hv = hc/\lambda$$

$$\frac{6.626\times10^{-34}\mathrm{m^2kg\,s^{-1}}}{8(9.109\times10^{-31}\mathrm{kg})(1.34\times10^{-10}\mathrm{m})^2}(4-1) = \frac{2.998\times10^{8}\mathrm{m/s}}{\lambda}$$

$$\lambda = 1.97\times10^{-8}\ \mathrm{m} = 19.7\ \mathrm{nm}$$

(2) (3 points) Let's use the same model for 1,3-butadiene ($H_2C=CH-CH=CH_2$). Let's assume that we can ignore bond angles and find the size of the box by adding C=C and C-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 π electrons, HOMO and LUMO are n=2 and 3 levels, respectively.

$$\frac{6.626\times10^{-34}\mathrm{m^2kg\,s^{-1}}}{8(9.109\times10^{-31}\mathrm{kg})((1.34\times2\ +1.48)\times10^{-10}\mathrm{m})^2}(9-4) = \frac{2.998\times10^{8}\mathrm{m/s}}{\lambda}$$

$$\lambda = 1.14\times10^{-7}\ \mathrm{m} = 114\ \mathrm{nm}$$

(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 π system such as C=C-C=C, C=C-C=C-C=C, C=C-C=C-C=C-C=C, and so on. Assume that the light emission is associated with the LUMO → HOMO transition.

\>> As seen above, for the system that has n double bonds and thus 2n □ electrons, the HOMO-LUMO gap is E_{n+1}-E_n.

$$\lambda = \frac{2.998\times10^{8}\mathrm{m/s}}{\dfrac{6.626\times10^{-34}\mathrm{m^2kg\,s^{-1}}}{8(9.109\times10^{-31}\mathrm{kg})((1.34n\ +1.48\times(n-1))\times10^{-10}\mathrm{m})^2}(2n+1)}$$

For n = 1, λ = 19.7 nm

For n = 2, λ = 114 nm

For n = 3, λ = 229 nm

For n = 4, λ = 352 nm

For n = 5, λ = 477 nm; the minimum # of C=C bonds

For n = 6, λ = 605 nm; the maximum # of C=C bonds

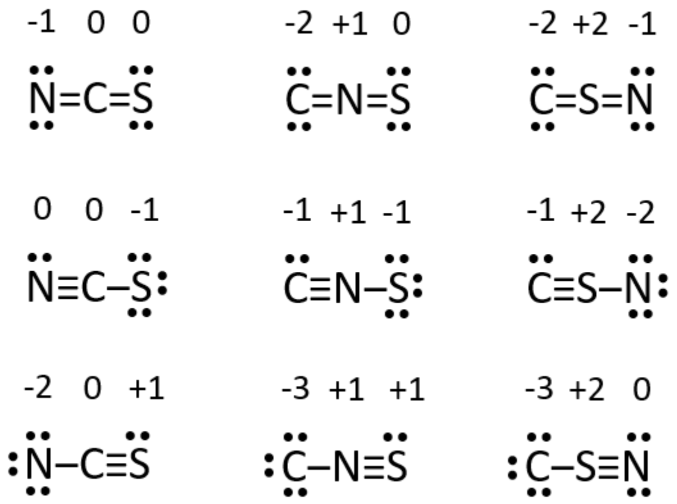
For n = 7, λ = 733 nm

8. (16 points)

To detect the presence of Fe(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 Fe-thiocyanate bond formation; N-bonding and S-bonding. To explain this phenomenon, let's consider Lewis structure for thiocyanate anion.

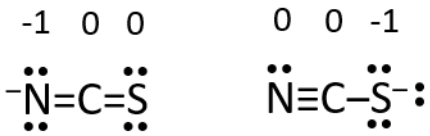
(1) (9 points) Draw all nine possible Lewis structures for a thiocyanate anion and write formal charges for each atom in each Lewis structure.

>>



(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 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.



N-bonding mode

Fe–N=C=S

S-bonding mode

N≡C–S–Fe

(3) To generate thiocyanate ions, the following reactions can be used.

(3-1) (2 points) $8CN^- + S_8 \rightarrow 8\ SCN^-$ (S-bonding mode structure)

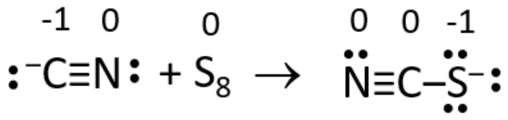
Which atom of the reactants is reduced and which atom is oxidized? Use formal charge changes.

(3-2) (3 points) $CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$ (N-bonding mode structure)

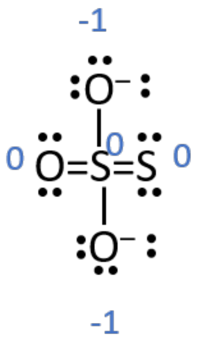
Draw the Lewis structures of $S_2O_3^{2-}$ and SO_3^{2-} ions and determine formal charges. Is this reaction a redox reaction or S atom transfer reaction? Rationalize your answer by using formal charges.

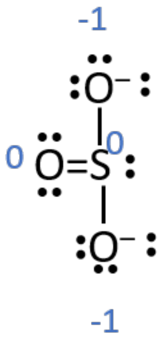
\>>

(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.





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 9.890×10^{-10} m show four peaks in which the electrons have speeds 7.992×10^{6} m s^{-1} (peak a), 2.046×10^{7} m s^{-1} (peak b), 2.074×10^{7} m s^{-1} (peak c), and 2.009×10^{7} m 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 energy-level diagram of sodium based on photoelectron spectroscopy findings.

(a) The ground-state electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$.

(b) The energy of the X-rays is

$$E_{X-ray} = h\nu = \frac{hc}{\lambda} = \frac{(6.62607 \times 10^{-34}\text{ J s})(2.99792 \times 10^{8}\text{ m } s^{-1})}{9.890 \times 10^{-10}\text{ m}} = 2.0085\times10^{-16}\text{ J}$$

$$= 2.0085 \times 10^{-16}\text{ J}\left(\frac{1\text{ eV}}{1.6022 \times 10^{-19}\text{ J}}\right) = 1253.6\text{ eV}$$

(c)

$$\text{KE} = \frac{1}{2} m_e v^2$$

$$\text{KE}_a = \frac{(9.10938 \times 10^{-31}\text{kg})(7.992 \times 10^{6}\text{ m s}^{-1})^2}{2}\left(\frac{1\text{ eV}}{1.6022 \times 10^{-19}\text{ J}}\right) = 181.6\text{ eV}$$

$$\text{KE}_b = \frac{(9.10938 \times 10^{-31}\text{kg})(2.046 \times 10^{7}\text{ m s}^{-1})^2}{2}\left(\frac{1\text{ eV}}{1.6022 \times 10^{-19}\text{ J}}\right) = 1190.0\text{ eV}$$

$$\text{KE}_c = \frac{(9.10938 \times 10^{-31}\text{kg})(2.074 \times 10^{7}\text{ m s}^{-1})^2}{2}\left(\frac{1\text{ eV}}{1.6022 \times 10^{-19}\text{ J}}\right) = 1222.8\text{ eV}$$

$$\text{KE}_d = \frac{(9.10938 \times 10^{-31}\text{kg})(2.009 \times 10^{7}\text{ m s}^{-1})^2}{2}\left(\frac{1\text{ eV}}{1.6022 \times 10^{-19}\text{ J}}\right) = 1147.4\text{ eV}$$

(d)

$$\text{IE} = \text{E}_{\text{X-ray}} - \text{E}_\text{k}$$

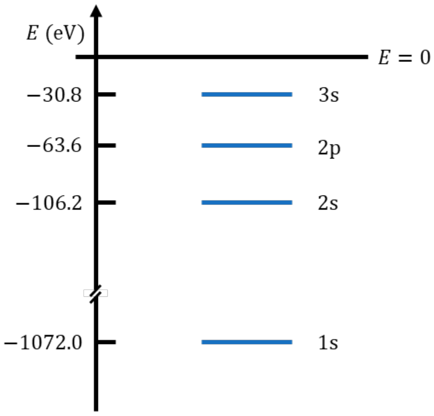
$$\text{IE}_\text{a} = 1253.6\text{ eV} - 181.6\text{ eV} = 1072.0\text{ eV}$$

$$\text{IE}_\text{b} = 1253.6\text{ eV} - 1190.0\text{ eV} = 63.6\text{ eV}$$

$$\text{IE}_\text{c} = 1253.6\text{ eV} - 1222.8\text{ eV} = 30.8\text{ eV}$$

$$\text{IE}_\text{d} = 1253.6\text{ eV} - 1147.4\text{ eV} = 106.2\text{ eV}$$

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


E (eV)
E = 0
−30.8
3s
−63.6
2p
−106.2
2s
−1072.0
1s

Physical Constants

Avogadro's number	N_A = 6.02214179 x 10^{23} mol^{-1}
Bohr radius	a_0 = 0.52917720859 Å = 5.2917720859x10^{-11} m
Boltzmann's constant	K_B = 1.3806504 x 10^{-23} J K^{-1}
Electronic charge	e = 1.602176487 x 10^{-19} C
Faraday constant	F = 96485.3399 C mol^{-1}
Masses of fundamental particles:	
Electron	m_e = 9.10938215 x 10^{-31} kg
Proton	m_P = 1.672621637 x 10^{-27} kg
Neutron	m_n= 1.674927211 x 10^{-27} kg
Permittivity of vacuum	ε_o = 8.854187817 x 10^{-12} C^{-2} J^{-1} m^{-1}
Planck's constant	h = 6.62606896 x 10^{-34} J s
Ratio of proton mass to electron mass	m_P / m_e = 1836.15267247
Speed of light in a vacuum	c = 2.99792458 x 10^{8} m s^{-1} (exactly)
Standard acceleration of terrestrial gravity	g = 9.80665 m s^{-2} (exactly)
Universal gas constant	R = 8.314472 J mol^{-1} K^{-1}
	= 0.0820574 L atm mol^{-1} K^{-1}

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

Conversion factors

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

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

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985) — 13
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986) — IIIA
ATOMIC NUMBER — 5
RELATIVE ATOMIC MASS (1) — 10.811
SYMBOL — **B**
ELEMENT NAME — BORON

PERIOD	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** **Lanthanide**	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** **Actinide**	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netlinx.com)

Claim Form for General Chemistry Examination

Page (/)

Class:__________, Professor Name:___________, I.D.# :_____________, Name:______________________

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