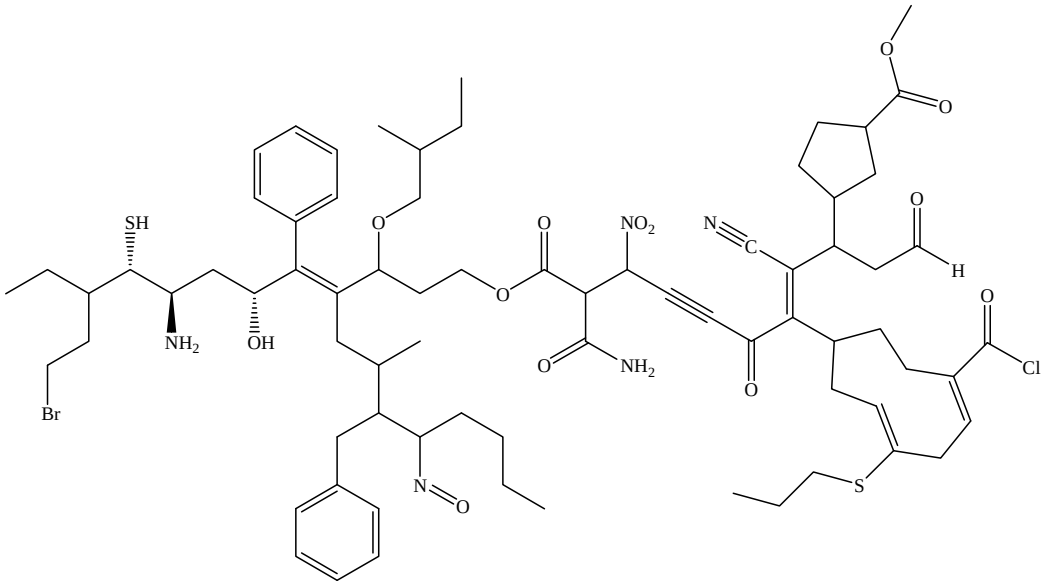
Chem 201 Midterm
Fall, 2018
Beauchamp Name _____

| Problems | Points | Credit |
|---|---|---|
| 1. Functional Group Nomenclature (1 large structure) | 30 | |
| 2. Resonance, Formal Charge, Arrows | 18 | |
| 3. Cyclohexane Conformations, Newman Projections | 30 | |
| 4. Newman Projections, Conformational Energies | 25 | |
| 5. Stereochemical Analysis | 30 | |
| 6. 3D Structure, Resonance, Hybridization, Angles, Shapes (1) | 36 | |
| 7. 2D Lewis Structures (1, large) | 25 | |
| 8. Functional Groups, Names or Types of Isomers or Special Types of Carbons and Substituents, Degrees of Unsaturation | 28 | |
| 9. Forces of Interaction and Physical Properties | 19 | |
| 10. Properties of Atoms, (ionization potential, $Z_{eff}$, radii, electronegativity), Logic Arguments of Organic Chemistry (inductive, resonance, steric) | 26 | |
| Total | 267 | |

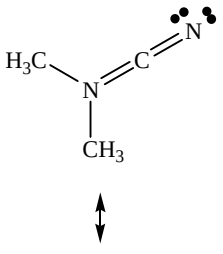
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Partial credit is given for any partially correct responses. Do your best to show me what you know in the time available.

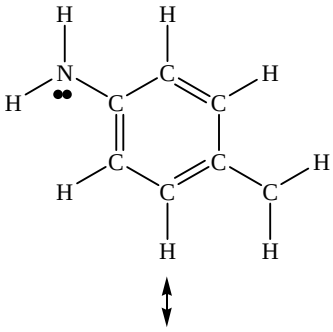
The wise does at once what the fool does at last. Baltasar Gracian

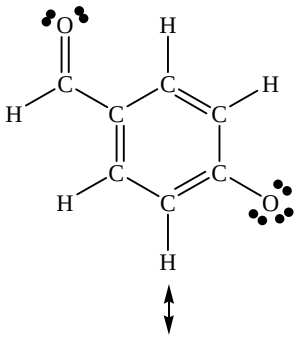
1. Provide an acceptable name for the following molecule. Only specify R and S where shown as 3D. (30 pts)




2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the **best** other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent with a brief reason why. (18 pts)



3. Draw all possible chair conformations of trans-1- methoxy-3-isopropylcyclohexane. The axial energy of a methoxy group is 0.6 kcal/mole and the axial energy of isopropyl is 2.1 kcal/mole. The gauche energy of methoxy/isopropyl is 0.9 kcal/mole. Make the left most ring carbon $C_1$ and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projection of the least stable conformation using the $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ bonds to sight along. Point out any gauche interactions of the substituents shown in your Newman projection. Sketch an energy diagram that shows how the energy changes (lower to higher) with the conformational changes and estimate the ratio of the two conformations at equilibrium. Show your work.

a. (15 pts)

conformation 1 conformation 2

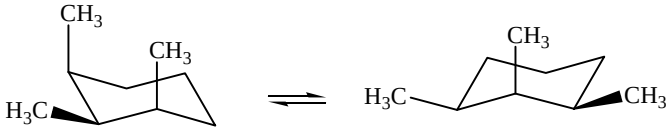
b. Newman projection ($C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ ) – least stable, point out any gauche interactions with the substituent(s). (5 pts)

c. Energy diagram and relative percents ($K_{eq}$ = ?) (5 pts)

$$K = 10^{\frac{-\Delta H}{2.3RT}}$$

R = 2 cal/mol-K
T = 300 K

d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a $K_{eq}$. (Assume R = 2 cal/mol-K and T = 300 K.) Use energy values provided in the box. Show your work. (5 pts)




One axial methyl group = +1.7 kcal/mole,
Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,
Three axial methyl groups, on the same side = +12.9 kcal/mole and
1,2 gauche methyl groups = 0.8 kcal/mole.

ΔH ≈

$K_{eq}$ ≈

4. Use a Newman projection of the C3→C4 bond of 2,2,3-trimethyl-4-phenylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the tables below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Calculate a ratio of least stable to most stable based on ΔH values. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection, then decide your line of sight. (25 pts)

2D Structure

Approximate Eclipsing Energy Values (kcal/mole)
Some were estimated by me.

| | H | Me | Et | i-Pr | t-Bu | Ph | Br |
|---|---|---|---|---|---|---|---|
| H | 1.0 | 1.4 | 1.5 | 1.6 | 3.0 | 1.7 | 1.6 |
| Me | 1.4 | 2.5 | 2.7 | 3.0 | 8.5 | 3.3 | 2.8 |
| Et | 1.5 | 2.7 | 3.3 | 4.0 | 10.0 | 3.8 | 3.1 |
| i-Pr | 1.6 | 3.0 | 4.0 | 7.8 | 13.0 | 8.1 | 3.6 |
| t-Bu | 3.0 | 8.5 | 10.0 | 13.0 | 23.0 | 13.5 | 9.1 |
| Ph | 1.7 | 3.3 | 3.8 | 8.1 | 13.5 | 8.3 | 4.2 |
| Br | 1.6 | 2.8 | 3.1 | 3.6 | 9.1 | 4.2 | 3.0 |

Approximate Gauche Energy Values (kcal/mole)
Some were estimated by me.

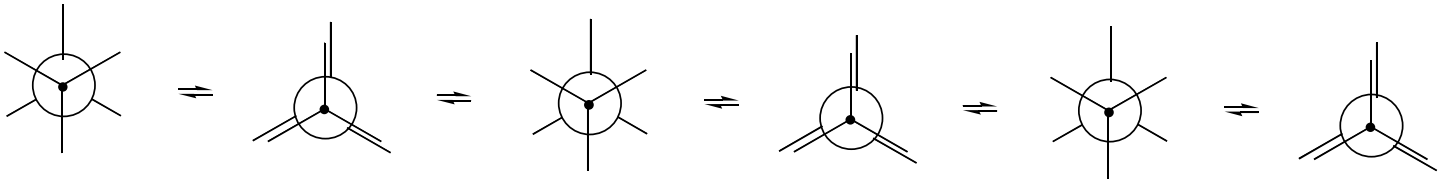
| | H | Me | Et | i-Pr | t-Bu | Ph | Br |
|---|---|---|---|---|---|---|---|
| H | 0 | 0 | 0.1 | 0.2 | 0.5 | 0.2 | 0.1 |
| Me | 0 | 0.8 | 0.9 | 1.1 | 2.7 | 1.4 | 1.0 |
| Et | 0.1 | 0.9 | 1.1 | 1.6 | 3.0 | 1.7 | 1.2 |
| i-Pr | 0.2 | 1.1 | 1.6 | 2.4 | 3.5 | 2.1 | 1.6 |
| t-Bu | 0.5 | 2.7 | 3.0 | 3.5 | 7.2 | 3.9 | 3.3 |
| Ph | 0.2 | 1.4 | 1.7 | 2.1 | 3.9 | 2.7 | 1.9 |
| Br | 0.1 | 1.0 | 1.2 | 1.6 | 3.3 | 1.9 | 1.1 |

$\Delta G \approx \Delta H$

$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

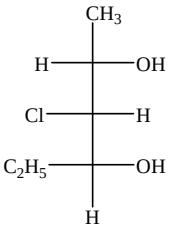
Newman projections:

lowest PE

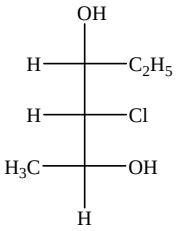



$K_{eq}$ calculation

5. Use the following set of Fischer projections to answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (30 pts)




(3 pts) A

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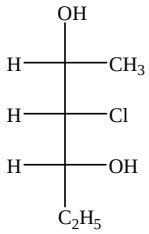
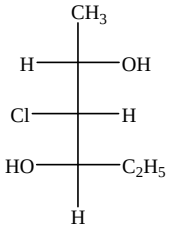
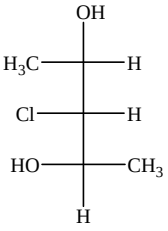



C




D




E

a. Which are optically active? A B C D E

b. Which are meso? A B C D E (17 pts)

c. Which is not an isomer with the others? A B C D E

d. Which pairs are enantiomers? AB AC AD AE BC BD BE CD CE DE

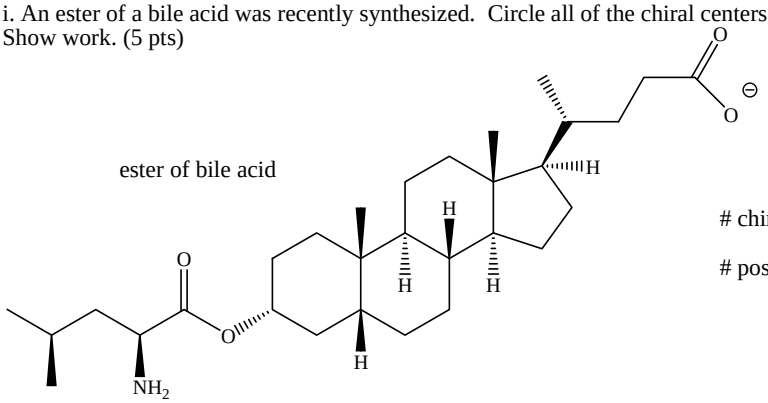
e. Which pairs are identical? AB AC AD AE BC BD BE CD CE DE

f. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE

g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BC BD BE CD CE DE

h. Draw any stereoisomers of 3-chloroohexan-2,4-ol as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)

i. An ester of a bile acid was recently synthesized. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)



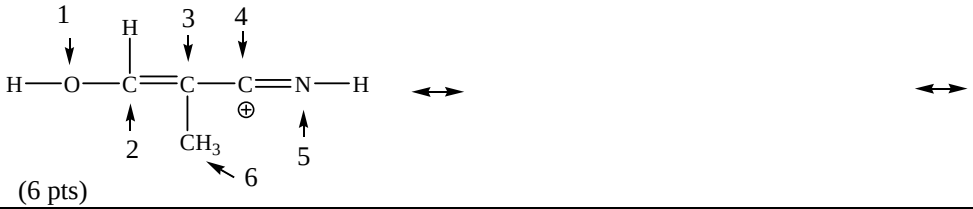

ester of bile acid

chiral centers are $sp^3$ atoms with 4 different groups attached

# chiral centers = _____

# possible stereoisomers = _____

6. Draw two additional "**better**" 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets unless + is written next to carbon. Add in any necessary lone pairs and use proper curved arrows to show electron movement. Which structure(s) is(are) best and why? Draw a 3D structure **for the given resonance structure**. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms in the **given** structure. (30 pts)




(6 pts)

(14 pts)

Use the given (first) Lewis structure to answer this part. (12 pts)

| Atom | Shape | Hybridization | Bond Angles | # sigma bonds | # pi bonds | # lone pairs |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | | | | | |
| 6 | | | | | | |

Explain the different C-F bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of the fluorine atom in A and B? (4 pts)

A 


108 kcal/mole

B 

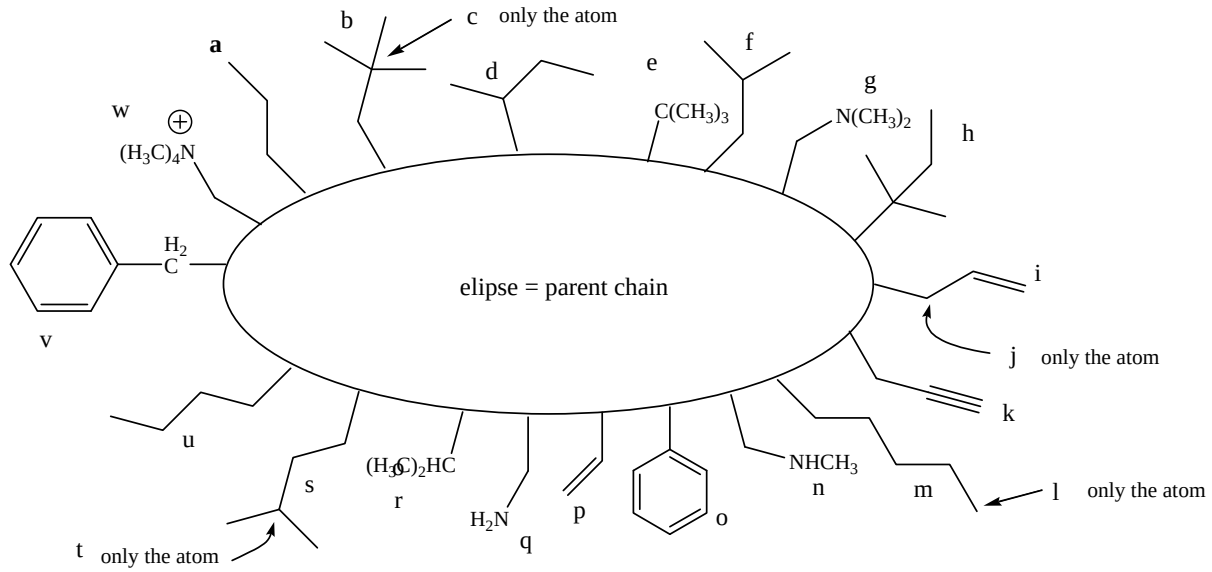

120 kcal/mole

7. Draw an acceptable Lewis structure (2D) for the following structure. Show all single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atom where present. (20 pts)

formal charge → 6 carbon ring →

$(CH_3)_2NOCCHC(CH_3)CHBrCHOHCO_2CH_2CCCOCHNO_2CHNH_2CH(OCH_3)CH(COCH_3)CH_2NHC_6H_4CH(CO_2H)CH(COCl)CHO$

8. Match each letter with its common name. Some letters may be used twice. (25 pts)

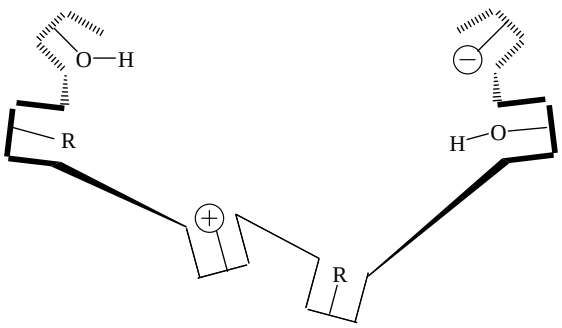



| | | | | |
|---|---|---|---|---|
| 1° carbon atom _____ | methylene _____ | isobutyl _____ | neopentyl _____ | allyl _____ |
| 2° carbon atom _____ | methine _____ | sec-butyl _____ | 1° amine _____ | vinyl _____ |
| 3° carbon atom _____ | n-propyl _____ | t-butyl _____ | 2° amine _____ | benzyl _____ |
| 4° carbon atom _____ | isopropyl _____ | n-pentyl _____ | 3° amine _____ | phenyl _____ |
| methyl _____ | n-butyl _____ | isopentyl _____ | 4° ammonium ion _____ | propargyl _____ |
| | | t-pentyl _____ | | |

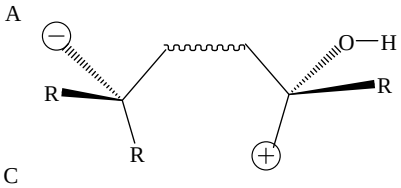
Use the given molecular formula to calculate the degree of unsaturation. Show work. $C_{21}H_{24}BrClFN_3O_5$, (3 pts)

9. a. The active site of an important liver enzyme has just been discovered. Several key regions are shown in the enzyme active site, just below. As an employee of Bronco Pharmaceutical, you are trying to design an inhibitor molecule that will strongly bind to the key regions of the active site so that the normal substrate cannot get in and react. Four possible inhibitors are shown below. Pick the molecule you think will block the enzyme cavity the best and draw it in the active site. Dashes represent "behind" the page, heavy lines indicate in "front" of the page and simple lines are "in" the page. R represents a nonpolar group. Give a very brief explanation for why your choice will work best. (7 pts)

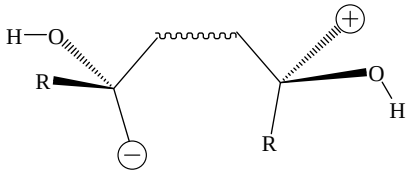
Enzyme active site




A




B

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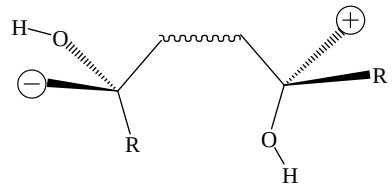
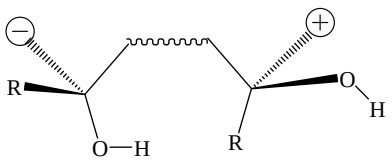
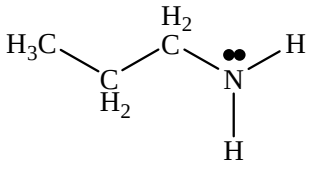
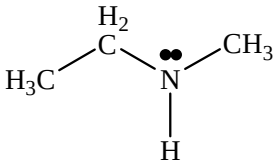


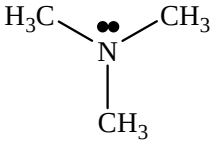

D



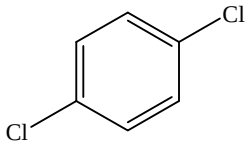

b. Propyl amine, ethylmethylamine and trimethyl amine have boiling points of 7°C, 35°C and 51°C. Match each temperature with the correct compound and provide an explanation for you answer. (7 pts)



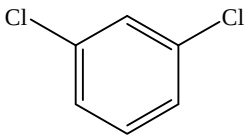




c. 1,3-dichlorobenene and 1,4-dichlorobenzene have melting points of -22 and 53°C, in no particular order. Match each temperature with the correct compound and provide an explanation for you answer. (5 pts)




1,4-dichlorobenzene

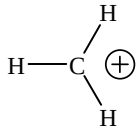



1,3-dichlorobenzene

10. Logic arguments of organic and biochemistry

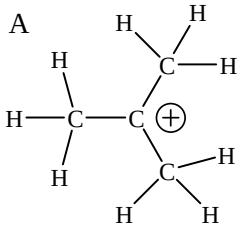
a. The first molecule in each row is a reference point. Explain if the indicated substitution will be stabilizing, destabilizing or have no effect relative to the reference structure. Provide an explanation for your answer. (10 pts)

i.



ref. structure

A



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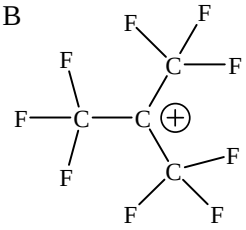
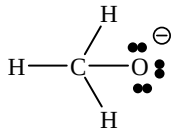
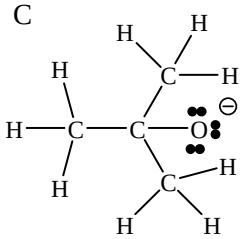


ii.

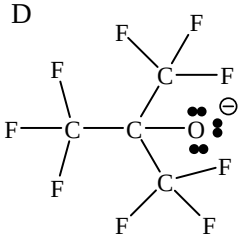


ref. structure

C



D



b. Which atom has the higher first ionization potential and why? (F or S) (16 pts, 4 pts each)

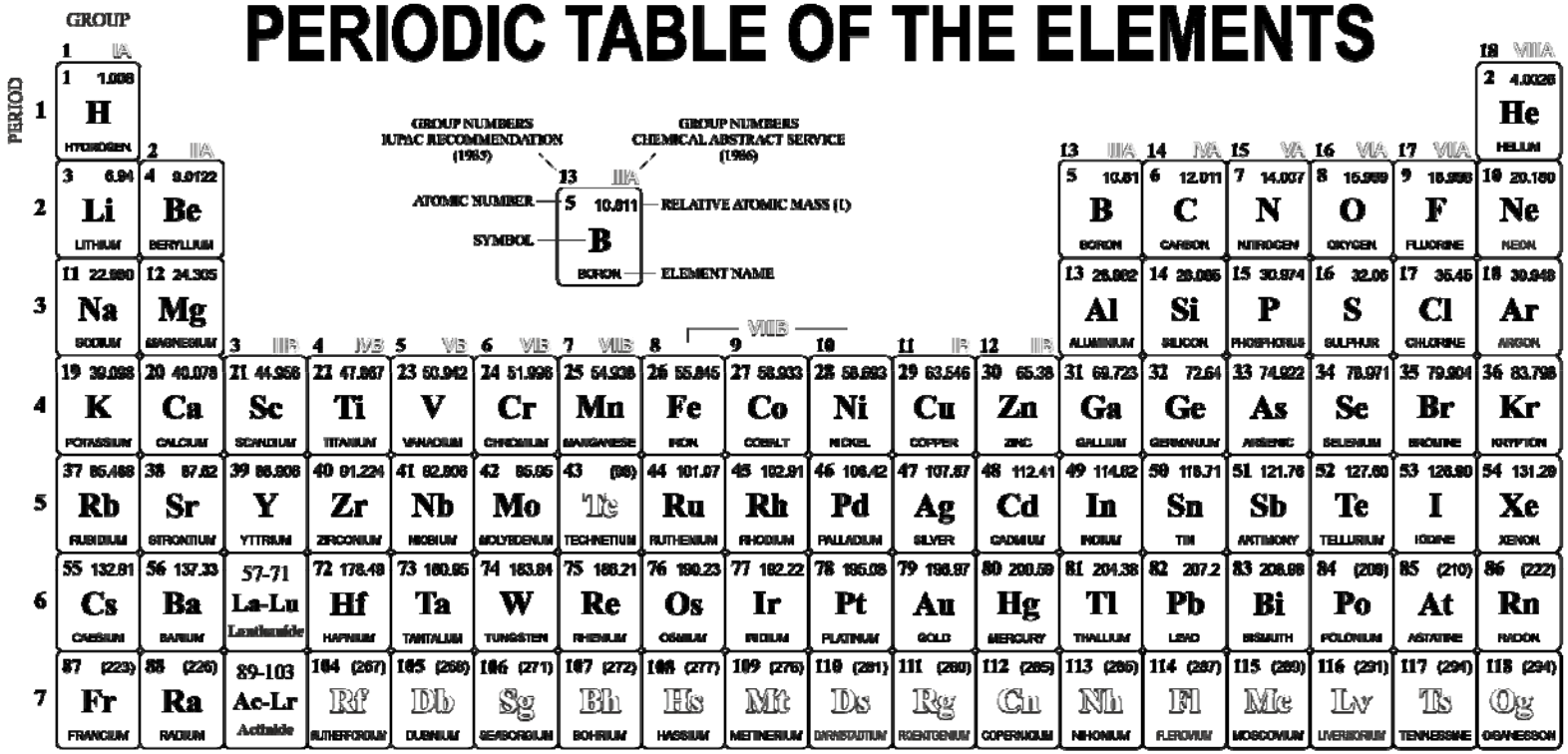
c. Which neutral atom has the larger atomic radius and why? (S or Cl)

d. Which anion has the larger radius and why? ($Br^{-1}$ or $Se^{-2}$)

e. Which cation has the larger radius and why? ($Na^{+}$ or $Mg^{+2}$)

You can't build a reputation on what you are going to do. Henry Ford

# PERIODIC TABLE OF THE ELEMENTS






LANTHANIDE

| 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 138.91 | 140.12 | 140.91 | 144.24 | (145) | 150.36 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.05 | 174.97 |
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| LANTHANUM | CERIUM | PRASEODYMIUM | NEODYMIUM | PROMETHIUM | SAMARIUM | EUROPIUM | GADOLINIUM | TERBIUM | DYSPROSIUM | HOLMIUM | ERBIUM | THULIUM | YTTERBIUM | LUTETIUM |

ACTINIDE

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

www.periodni.com

(1) Atomic weights of the elements 2013, Pure Appl. Chem., 88, 265-291 (2016)