NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

9:30 – 10:45 am, August 8, 2013

Final Exam

There will be two ways that you can pick up your graded Final Exam:

- You can pick up your graded exam from Andy at office hours that he will hold on Monday, August 6th (9:30-10:30 am) at Coffman Union Starbucks.
- Alternately, you will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Monday, August 6th at noon. Exams that are not picked up within two weeks will be disposed of.

A periodic table, a chart of reaction conditions, and a table of typical NMR chemical shifts are attached to the back of this exam as aids. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

Right now, write your name and student ID number at the top of this page. When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

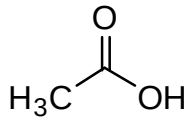
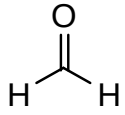
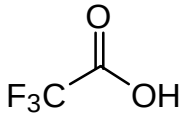
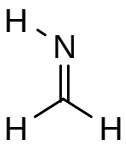
Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

NAME _____

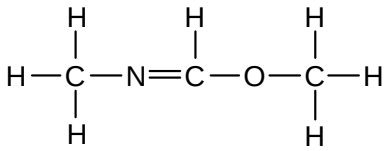
Scoring:		
	1. _____ / 14	6. _____ / 9
	2. _____ / 14	7. _____ / 15
	3. _____ / 39	8. _____ / 18
	4. _____ / 20	9. _____ / 12
	5. _____ / 9	

Total Score: _____ / 150

1. (14 pts) For each of the pairs of acids (or bases) below,
   - Draw the conjugate base (or acid).
   - Circle whether you think the first acid (or base) is more or less acidic (or basic) than the second.

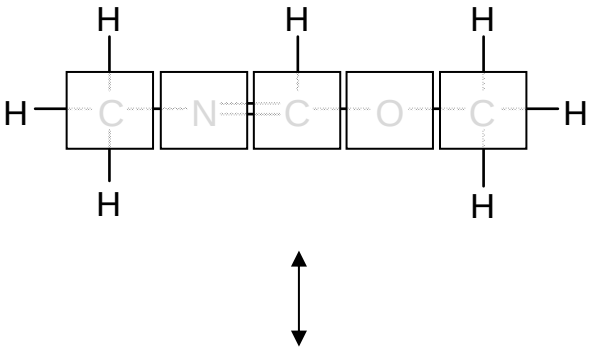
Acid	Conjugate Base	Base	Conjugate Acid
			
is		is	
MORE ACIDIC **LESS ACIDIC**		**MORE BASIC** **LESS BASIC**	
than		than	
			

2. (14 pts) For the molecule drawn at right, in the boxes provided:



- Draw all significant resonance structures. In each structure, draw all atoms, bonds, lone pairs of electrons, and formal charges.
- Draw a Lewis wedge/dashed-bond structure that illustrates the most stable three-dimensional conformation of the molecule. Draw all atoms, bonds, and charges, but omit lone pairs.
- In the boxes provided, write the hybridization state on any atom heavier than hydrogen.

atom hybridizations:

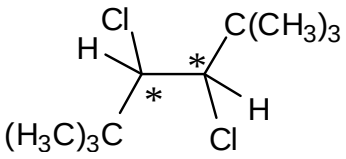


3-dimensional representation

resonance structure

resonance structure

3. (39 pts) The molecule below has two chiral centers (marked with asterisks) and three stereoisomers; one stereoisomer is achiral (*meso*), and two are chiral. Each stereoisomer reacts with $NaOCH_3$ via E2 elimination to yield, selectively, a single alkene product.



(a) I have drawn the molecule on the previous page entirely in the plane of the page, without any stereochemical information. **Using wedge and dashed-bond lines**, draw the achiral stereoisomer and one of the two chiral stereoisomers as three-dimensional structures. Then, **label each stereocenter** in your structures "(*R*)" or "(*S*)".

achiral (meso) stereoisomer

chiral stereoisomer

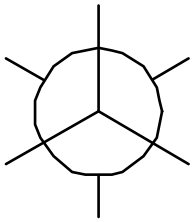
(b) What is the stereochemical relationship between the two molecules you drew above? Are they

enantiomers *or* **diastereomers** *or* **neither** ?

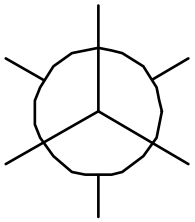
(Circle one answer.)

(c) E2 elimination requires a very specific geometric relationship between the leaving group and the proton being taken by the incoming base. In the boxes below, draw a Newman projection for each of the stereoisomers you drew above that puts the proton and leaving group in the right orientation to undergo E2. Then, "push arrows" on each diagram to illustrate the mechanism of the E2 elimination.

E2-reactive conformer for achiral (meso) stereoisomer



E2-reactive conformer for chiral stereoisomer



(d) **Which alkene product will be generated via E2** from each of the two stereoisomers you drew?

achiral (meso) stereoisomer

↓ $NaOCH_3$

*An alkene ("product **A**")*

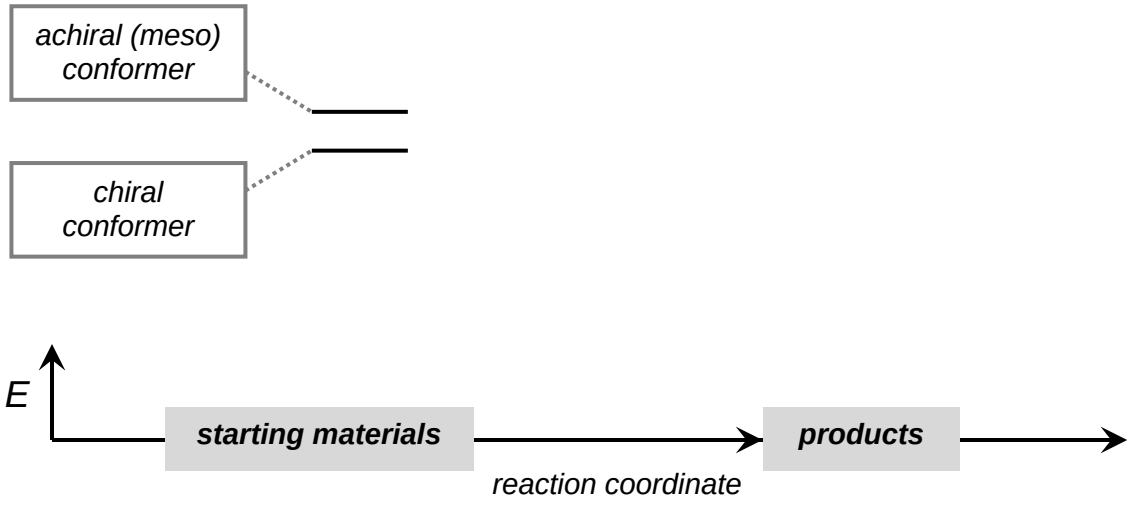
chiral stereoisomer

↓ $NaOCH_3$

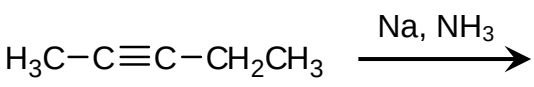
*A different alkene ("product **B**")*

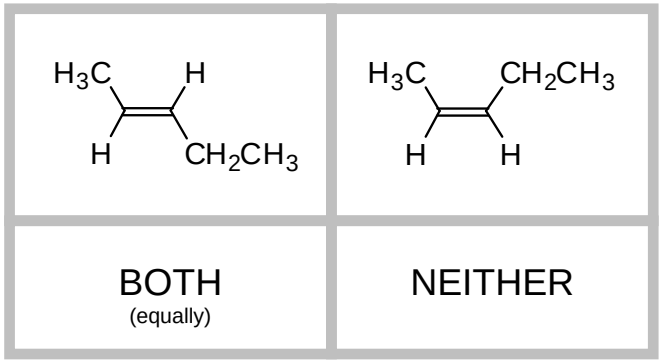
(e) On the potential energy diagram below, draw curves that represent the E2 elimination of each starting material to products **A** and **B**. The starting material energies have already been drawn for you (we will assume they are equal in energy)—you need to connect these starting points to transition state and product energies. Your curves should answer the following questions:

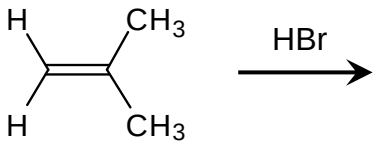
- Is product **B** higher, lower, or equal in energy relative to product **A**? Label your diagram so that it is clear which product energy level corresponds to which product.
- How many steps, and how many transition states, does each E2 pathway have?
- Is the overall activation energy for making product **B** larger, smaller, or equal to the activation energy for making product **A**?

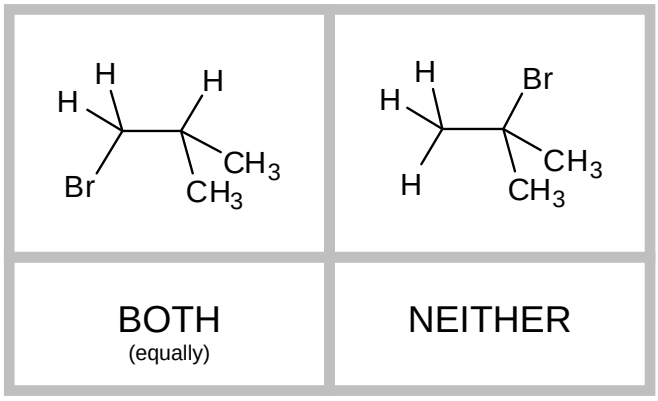


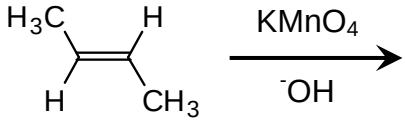
4. (20 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced <u>equally</u>, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

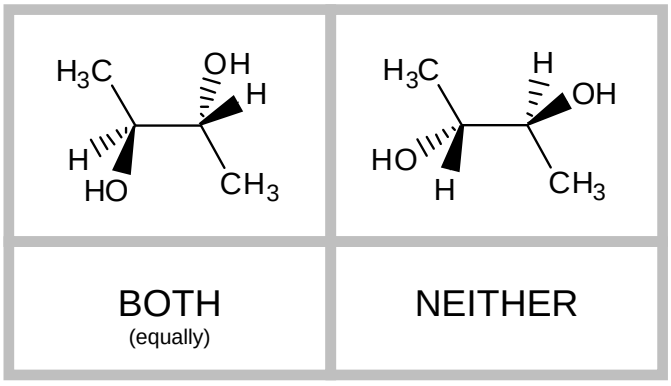


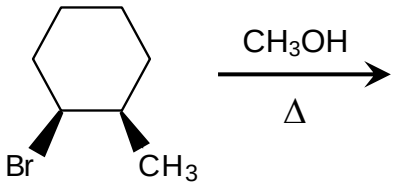


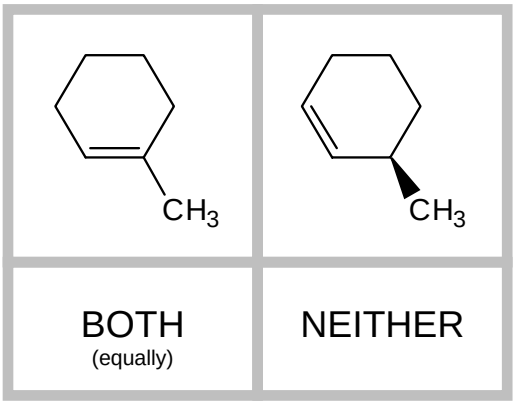


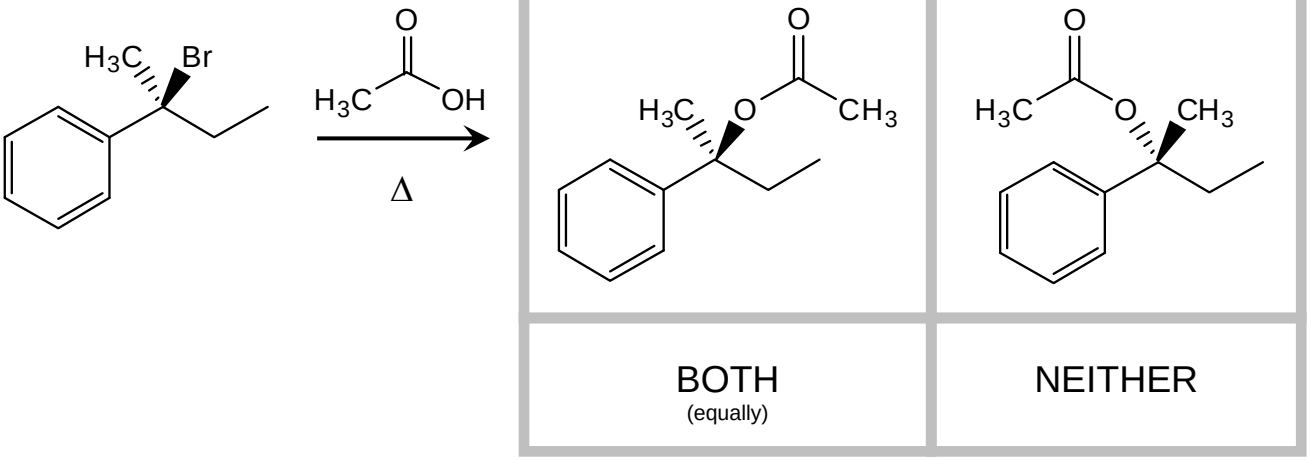




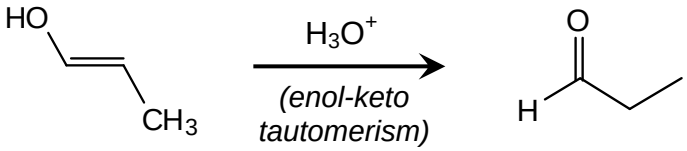






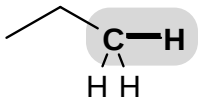
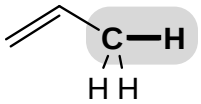


5. (9 pts) Draw a mechanism (using "electron pushing") for the reaction shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "H-A" as a generic acid.)

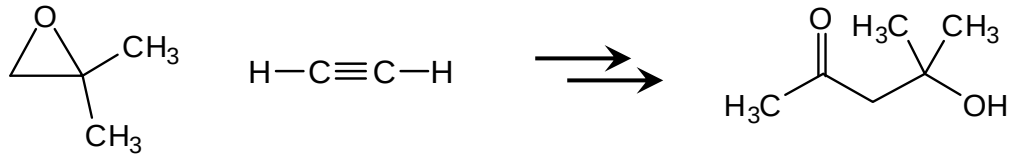


Mechanism:

6. (9 pts) Of the C-H bonds highlighted below, which:

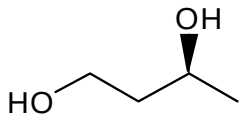
(check one box in each column)	has a larger bond dissociation energy?	is broken to form a more stable radical?	would be converted more rapidly to a C-Br bond by Br_2 and light?
	☐	☐	☐
	☐	☐	☐
NEITHER *(they are the same)*	☐	☐	☐

7. (15 pts) For the starting materials and product shown below, **propose a multistep synthesis**. In addition to the molecules shown, you can use any reagents and reactions we've learned about in class. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.

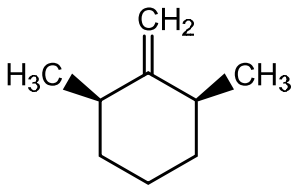


Multistep synthesis:

8. (18 pts) For each of the reactions on the following pages, fill in the empty box corresponding to the major product. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer box (e.g., by writing "+ enantiomer", etc.)



Swern oxidation →



*m*CPBA →

a chair conformer

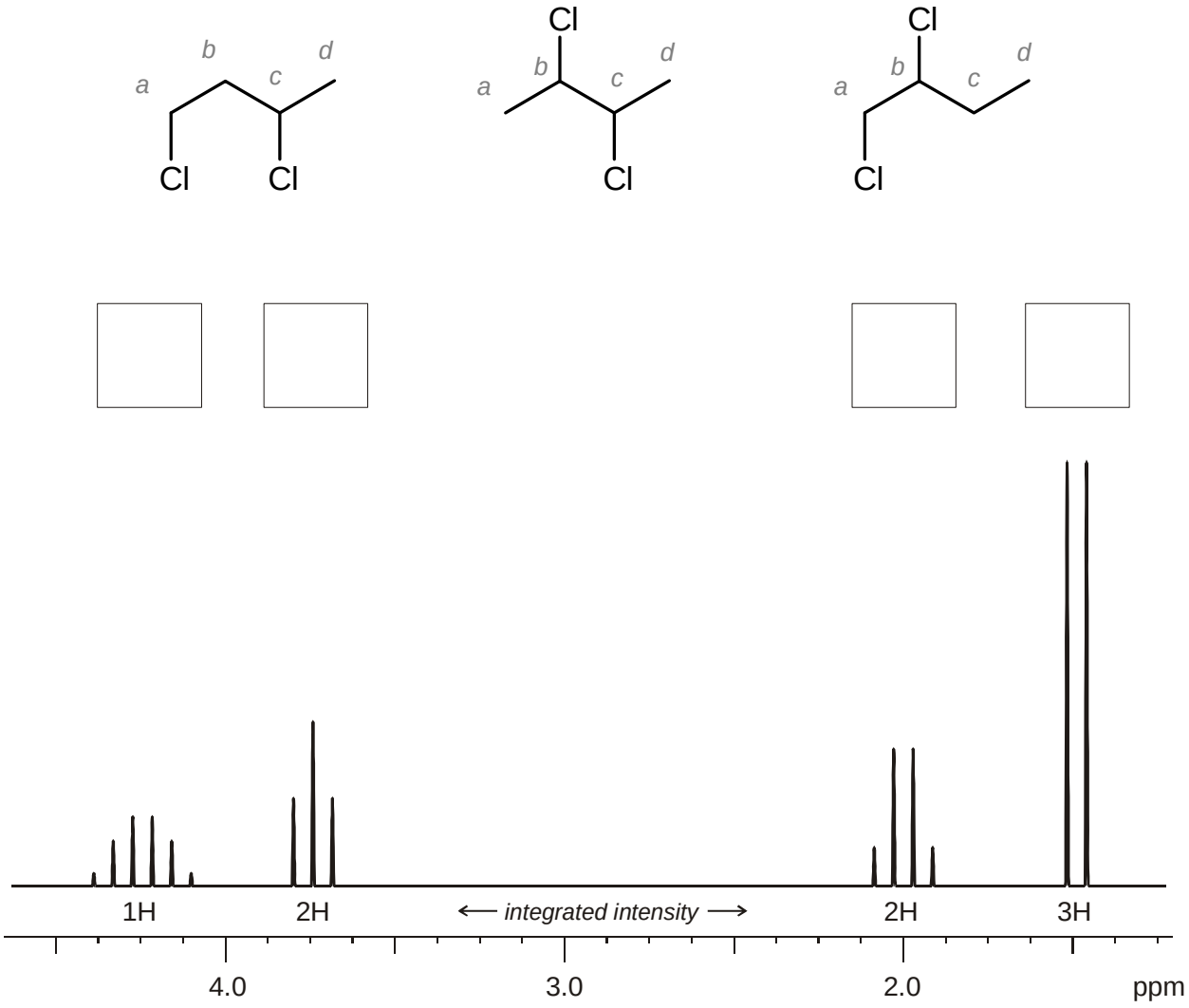
Special instructions for this part:

- Draw the preferred product as two equilibrating chair conformers (one per box). Feel free to omit H atoms from your structure.
- Indicate that one conformer is more stable than the other, or that they are equally stable, by circling the appropriate equilibrium arrow.

or *or* *(circle one)*

another chair conformer

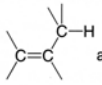
9. (12 pts) The ^{1}H NMR spectrum below corresponds to one of the following dichlorinated alkanes:

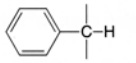


(a) Circle the molecule that would give this spectrum.

(b) The carbons of each candidate molecule structure are labeled “a” through “d”. Each multiplet in the NMR spectrum corresponds to H atoms attached to a single carbon atom. In the box above each multiplet, write the letter of the carbon that each peak’s H atoms are attached to.

^{1}H NMR Absorptions

Compound type	Chemical shift (ppm)
Alcohol	
	1–5
	3.4–4.0
Aldehyde	
	9–10
Alkane	0.9–2.0
RCH_3	~0.9
R_2CH_2	~1.3
R_3CH	~1.7
Alkene	
 sp^2 C–H	4.5–6.0
 allylic sp^3 C–H	1.5–2.5
Alkyl halide	
	4.0–4.5
	3.0–4.0
	2.7–4.0
	2.2–4.0
Alkyne	
—C≡C–H	~2.5

Compound type	Chemical shift (ppm)
Amide	
	7.5–8.5
Amine	
	0.5–5.0
	2.3–3.0
Aromatic compound	
 sp^2 C–H	6.5–8
 benzylic sp^3 C–H	1.5–2.5
Carbonyl compound	
 sp^3 C–H on the α carbon	2.0–2.5
Carboxylic acid	
	10–12
Ether 	3.4–4.0

^{13}C NMR Absorptions

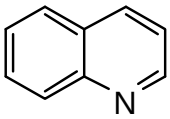
Carbon type	Structure	Chemical shift (ppm)
Alkyl, sp^3 hybridized C		5–45
Alkyl, sp^3 hybridized C bonded to N, O, or X	 Z = N, O, X	30–80
Alkynyl, *sp* hybridized C	—C≡C—	65–100
Alkenyl, sp^2 hybridized C		100–140
Aryl, sp^2 hybridized C		120–150
Carbonyl C		160–210

Final Exam Chart of Reaction Conditions

$Pt/H_2(g)$

$NaNH_2$

$Pd, BaSO_4$
$H_2(g)$



(quinoline)

$Na_2Cr_2O_7$
H_2SO_4

PBr_3

1. BH_3•THF
2. H_2O_2, OH^-

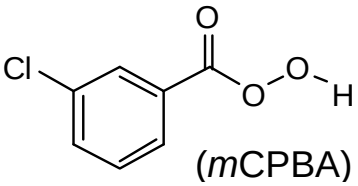
1. O_3
2. $(CH_3)_2S$

Na
NH_3

$HgSO_4$
H_2SO_4

1. $(COCl)_2$
   DMSO
   -60 °C
2. Et_3N
   (Swern oxidation)

H_2SO_4
H_2O



(*m*CPBA)

$KMnO_4$
(cold, dilute)
H_2O, OH^-

$SOCl_2$
pyridine

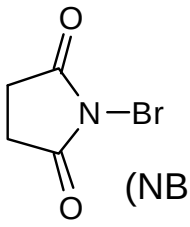
TsCl
pyridine

*m*CPBA
H_2O

1. O_3
2. H_2O

$KMnO_4$
H_2O, pH 7

Cl_2 *or* Br_2,
hν

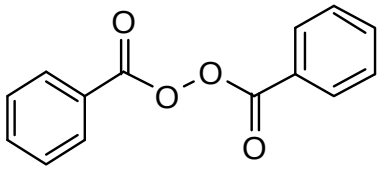


(NBS)

hν or AIBN

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

HBr



(benzoyl peroxide)

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01	2 2A																2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

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