NAME ________________________

ID # ________________________

ORGANIC CHEMISTRY II (2302)

8:00 – 8:50 am, August 2, 2016

Exam 4

If you want to pick this exam up Wednesday in class (in public), please check the box on the right: ☐

If you do not check the box, I will not bring your exam to class on Wednesday, and you will need to pick up your exam in private from Chemistry department staff in 115 Smith beginning Thursday, August 4th. Exams that are not picked up within two weeks will be disposed of.

A periodic table and a chart of amino acids and nucleic acid bases are attached to the back of this exam as an aid. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

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 ________________________

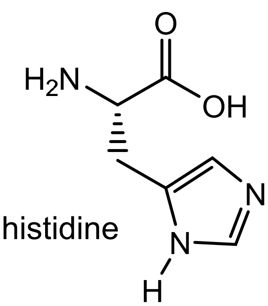
Scoring: 1. _________ / 24 4. _________ / 12

2. _________ / 26 5. _________ / 25

3. _________ / 13

Total Score: _________ / 100

1. (24 pts) L-Histidine is one of the twenty common amino acids. The imidazole side-chain of histidine is basic, and the conjugate acid of imidazole—imidazolium ion—has a pK_a = 6.9.

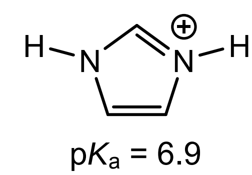


histidine

   a. Histidine can exist in different charge states, depending on solution pH. In the boxes below, draw three full chemical structures of histidine that you would expect to find at different pH values. Draw structures with a total charge of +1, 0, and -1.

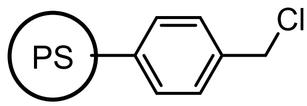
   b. What would you predict for the isoelectric point (pI) of histidine?

pI =



histidine, total charge = ***+1***	*histidine, total charge =* ***0***	*histidine, total charge =* ***-1***

   c. In the box on the next page, propose a multistep, solid-phase synthesis of alanyl histidine, (H_2N)-Ala-His-(COOH), starting from chloromethylated polystyrene. You do not need to draw any chemical structures to answer this problem; you can refer to molecules by name or chemical abbreviation. In addition to the starting materials shown at right, you can use any reagents and reactions we've learned about in class.



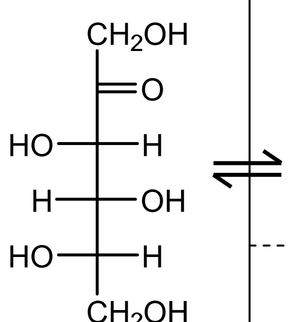
chloromethylated polystyrene

2. (26 pts) The acyclic structure of D-sorbose, an epimer of fructose, is shown below as a Fischer projection. This acyclic structure equilibrates with both 5-membered ring (furanose) and 6-membered ring (pyranose) forms.

   a. In the box on the right, draw the most stable 6-membered ring structure as a Haworth projection.

   b. Then, below that Haworth projection, draw the same ring as its most stable chair conformer. Your chair should have an axial -OH group at the anomeric carbon; this is the most stable anomer of sorbose.

   c. In your chair conformer, the axial -OH is stabilized by the “anomeric effect”, a



sorbose

cyclic D-sorbopyranose
(6-membered ring, Haworth projection)

(same ring, most stable chair conformer; include illustration of anomeric effect)

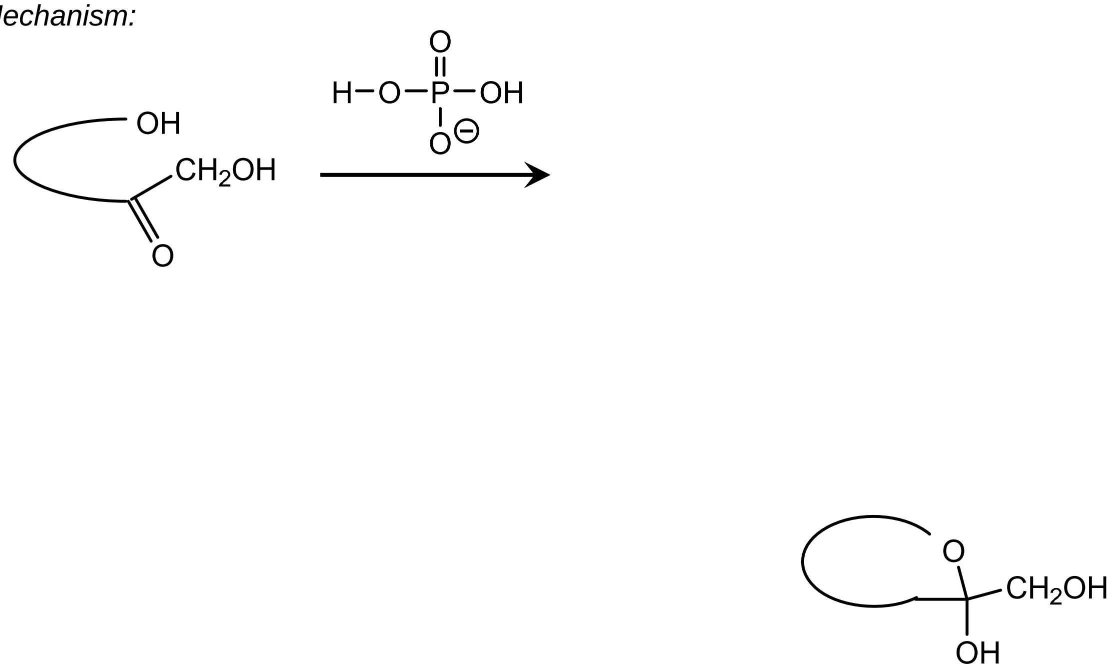
specific molecular orbital interaction. Illustrate that molecular orbital interaction on your drawing on the previous page, drawing lobes for orbitals.

d. In the box on this page at right, draw the 5-membered ring (furanose) structure as a Haworth projection.

cyclic α-D-sorbofuranose
(5-membered ring, Haworth projection)

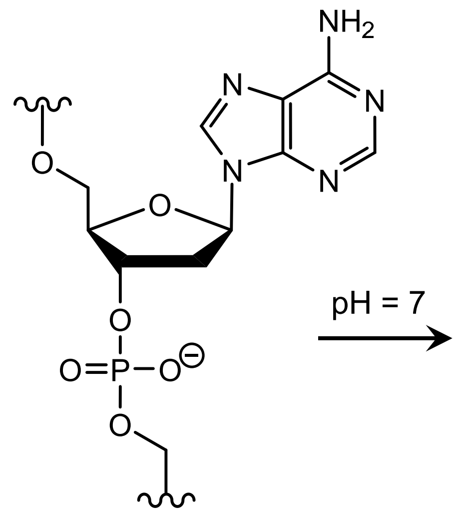
e. Acyclic and cyclic sorbose equilibrate spontaneously in acidic phosphate buffer. In the box below, draw a mechanism (using “electron pushing”) that illustrates how acyclic sorbose becomes cyclic sorbose under acid catalysis. Feel free to abbreviate the sugar backbone and any unchanged –OH functional groups as a cartoon loop or squiggle, as shown; you do not need to draw the entire sugar structure.

Mechanism:



3. (13 pts)
   a. A generic structure of an adenine nucleotide in DNA is shown on the next page. **Draw one change to that structure** so that it shows RNA instead. Draw directly onto my structure—there is no need to draw a whole new molecule.

b. This change makes RNA undergo intramolecular cleavage more rapidly than DNA. In the box on the right, draw the cyclic phosphate generated by RNA strand cleavage at pH = 7.



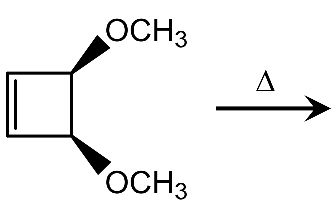
RNA cleavage product

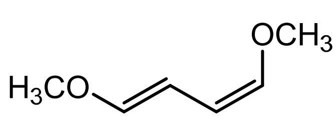
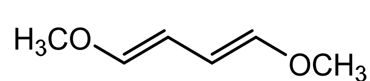
c. On the starting material above, add curved arrows to illustrate the first step in the mechanism of this cleavage reaction.

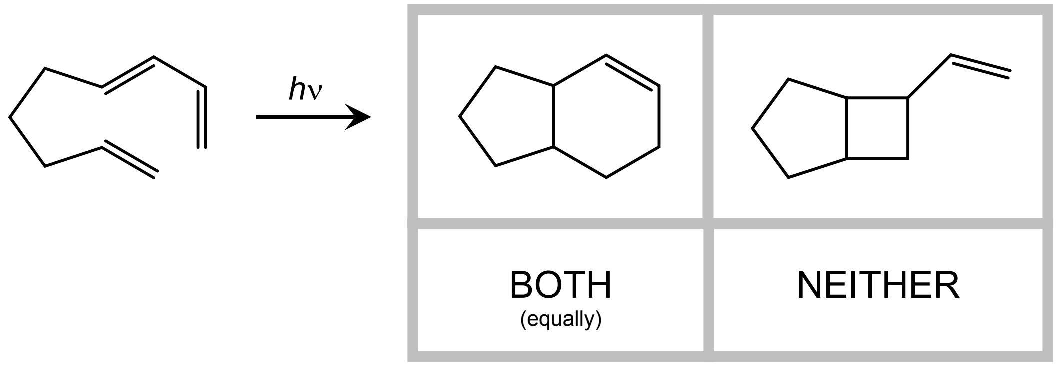
d. At pH = 7, which of the following statements about DNA and RNA is true?

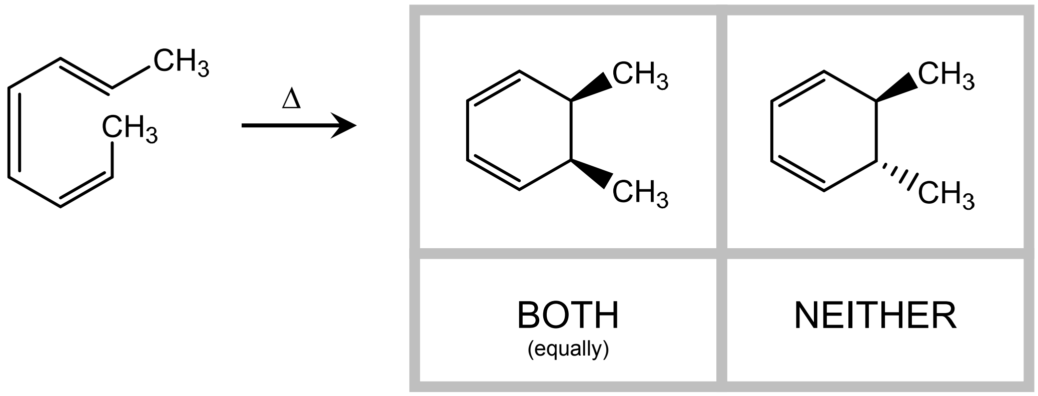
RNA is more stable than DNA. **RNA is less stable than DNA.** *or* **RNA and DNA are equally stable.** *(Circle one.)*

4. (12 pts) Each of the reactions below is drawn with two possible products. Circle the preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

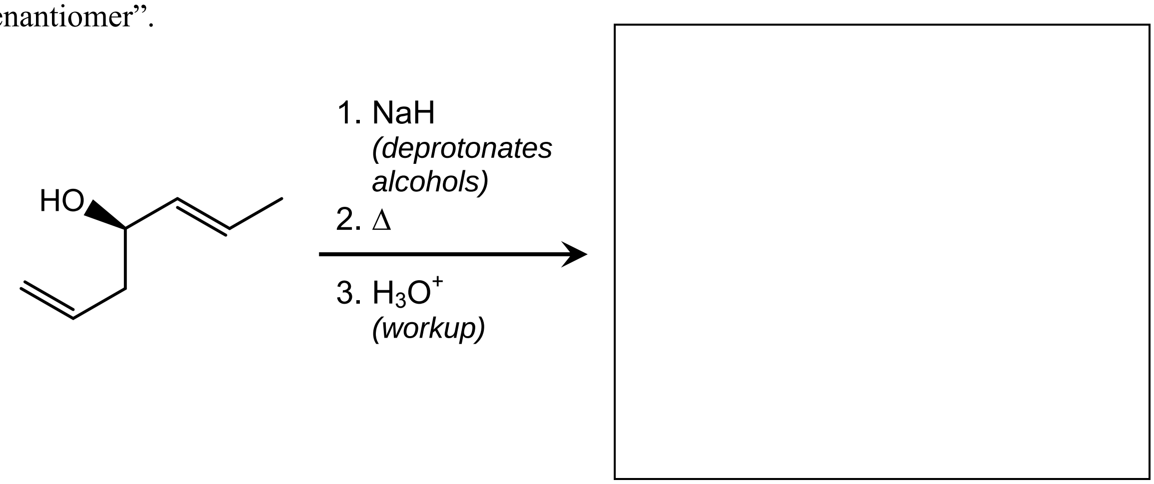


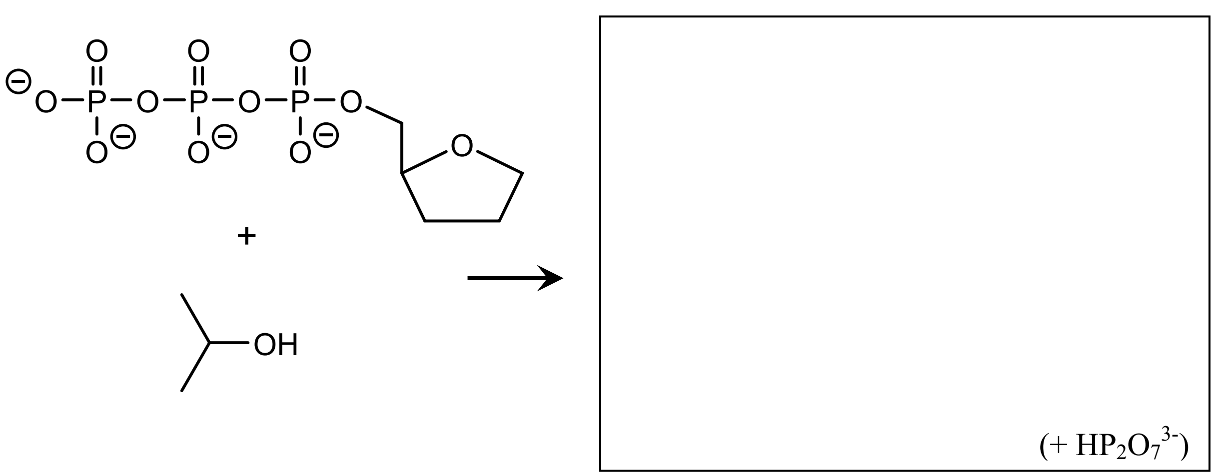
	
BOTH (equally)	NEITHER





5. (25 pts) For each of the reactions below and on the next page, fill in the empty box corresponding to reactants or product. Give only one answer in each box. For reactions that you expect to yield multiple products, draw one major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



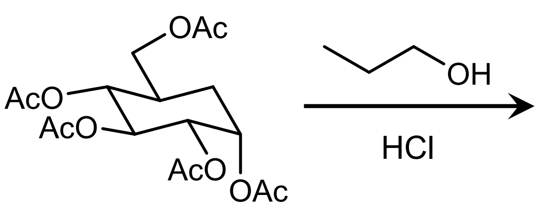


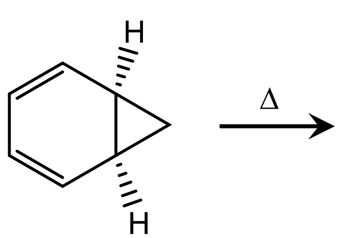
(H$_2$N)-Val-Phe-Pro-(COOH)
(a tripeptide)

1. PhNCS
2. H_3O^+, Δ

(Edman degradation)

*a dipeptide (do **not** use abbreviations)*





Exam 4 Chart of Reaction Conditions

Br_2
$FeBr_3$

Cl_2
$AlCl_3$

H_2SO_4
HNO_3

Sn *or* Fe
HCl/H_2O

H_2SO_4
SO_3

$KMnO_4$
^-OH, 100 °C

Mg
Et_2O

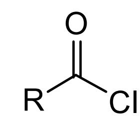
1. $NaNO_2$
   HCl
2. CuCN *or* H_3PO_2 *or* CuX *or* H_3O^+

R-X (R = alkyl)
$AlCl_3$ *or* $FeBr_3$

Zn(Hg),
HCl/H_2O

Li
hexane

H_2
Pd-C



$AlCl_3$

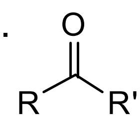
1. N_2H_4
2. KOH, Δ

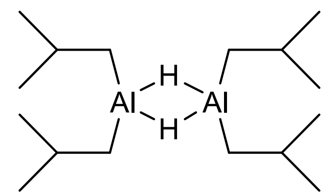
1. O_3
2. H_2O

RMgX

RLi

R_2CuLi

1. PPh_3
2. *n*-BuLi
3. 



(DIBAL-H)

$Na_2Cr_2O_7$
H_2SO_4

LiAlH(O*t*Bu)$_3$

1. Ag_2O
   NH_3
2. H_3O^+

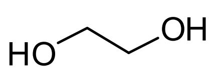
$Bu_4N^+F^-$

$PhCH_2Br$
Ag_2O

1. $LiAlH_4$
2. H_2O

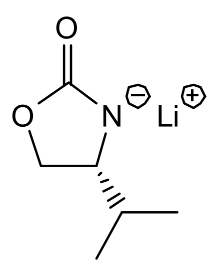
$(COCl)_2$

$(CH_3)_3SiCl$ {TMSCl},
or TBDMSCl;
Et_3N *or* imidazole

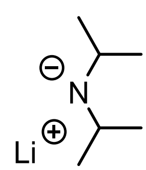


HCl

$NaNH_2$

1. 

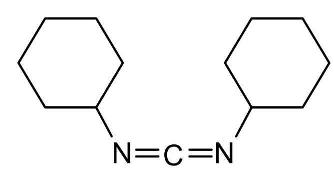
2. base
3. R-X
4. LiOH



(LDA)

$SOCl_2$
(& pyridine, usually)

1. $NaBH_4$
2. H_2O



(DCC)

$Pd(OAc)_2$
PPh_3, NEt_3

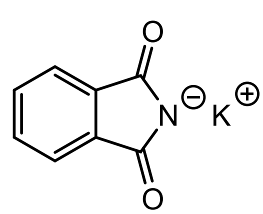
1. CH_3I
   (excess)
2. Ag_2O
   H_2O
3. Δ

$CHCl_3$
KO*t*Bu

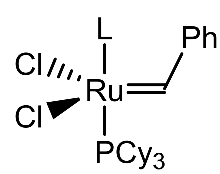
$Pd(PPh_3)_4$
NaOH

CF_3COOH

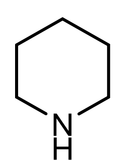
CH_2I_2
Zn(Cu)

1. 

2. N_2H_4 (or ^-OH)



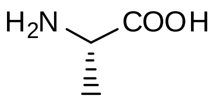
(Grubbs catalyst)

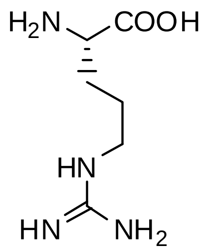


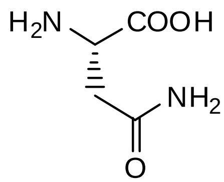
HF

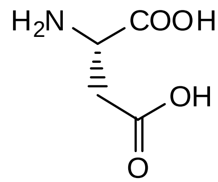
RCHO
$Na(OAc)_3BH$
or
$NaBH_3CN$

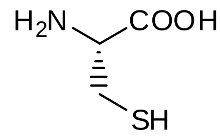
Exam 4 Chart of Amino Acids
(in Alphabetical Order)

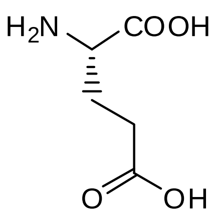

alanine
(Ala, A)

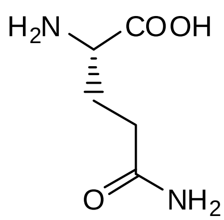

arginine
(Arg, R)

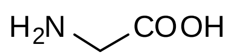

asparagine
(Asn, N)

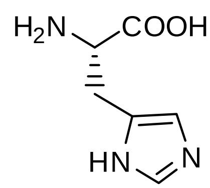

aspartic acid
(Asp, D)

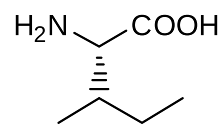

cysteine
(Cys, C)

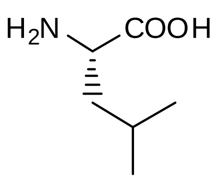

glutamic acid
(Glu, E)

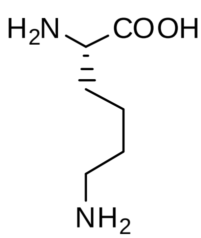

glutamine
(Gln, Q)

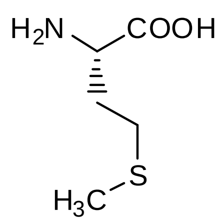

glycine
(Gly, G)

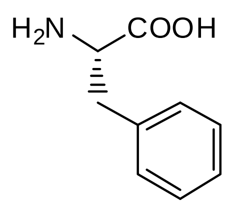

histidine
(His, H)

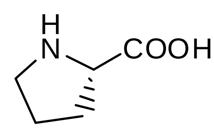

isoleucine
(Ile, I)

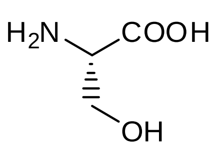

leucine
(Leu, L)

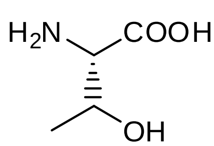

lysine
(Lys, K)

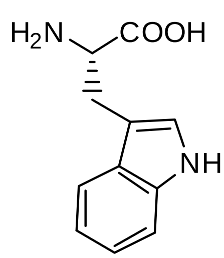

methionine
(Met, M)

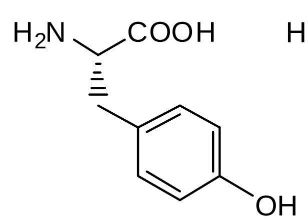

phenylalanine
(Phe, F)

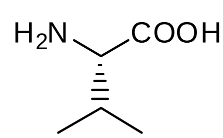

proline
(Pro, P)


serine
(Ser, S)

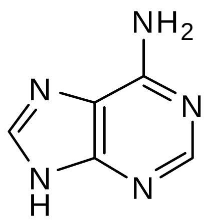

threonine
(Thr, T)


tryptophan
(Trp, W)

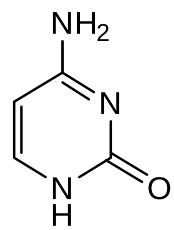

tyrosine
(Tyr, Y)


valine
(Val, V)

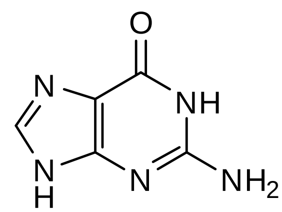
Exam 4 Chart of Nucleic Acid Bases
(in Alphabetical Order)



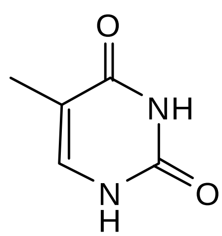
adenine
(A)



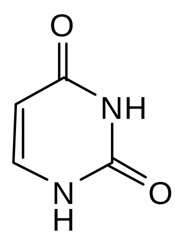
cytosine
(C)



guanine
(G)



thymine
(T)



uracil
(U)

Chemistry Reference Sheet

Key

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

Period	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01																	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											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)

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