NAME _____

ID # _____

ORGANIC CHEMISTRY II (2302)

12:20 – 1:10 pm, December 14, 2015

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, December 17th. Exams that are not picked up within two weeks will be disposed of.

A periodic table and charts of reagents and nucleic and amino acid structures 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).

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 _____

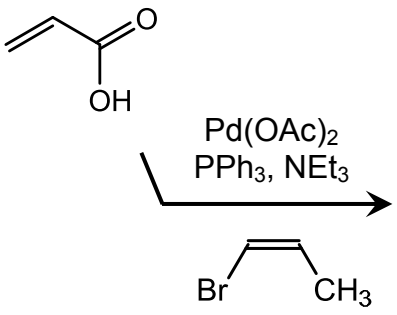
Scoring: 1. _____ / 16 4. _____ / 12

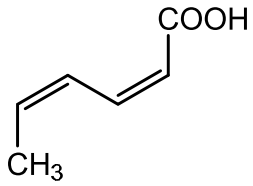
2. _____ / 23 5. _____ / 26

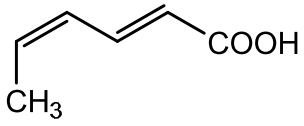
3. _____ / 23

Total Score: _____ / 100

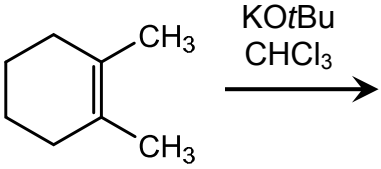
1. (16 pts) Each of the reactions below is drawn with two possible products or reactants. Circle the preferred product or set of reagents. If the two products are produced <u>equally</u>, or if either reaction would succeed, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

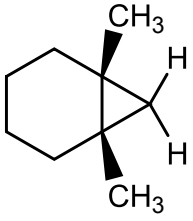


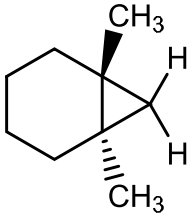




BOTH (equally)	NEITHER







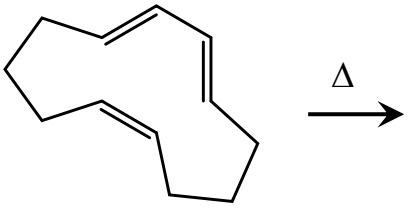
BOTH (equally)	NEITHER

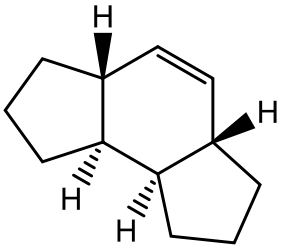
(H_2N)-Ala-Phe-Glu-(COOH)
(a tripeptide)

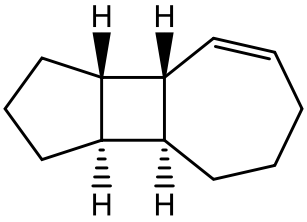
1. PhNCS
2. H_3O^+, Δ

(Edman degradation)

(H_2N)-Phe-Glu-(COOH) *(a dipeptide)*	(H_2N)-Ala-Phe-(COOH) *(a dipeptide)*
BOTH (equally)	NEITHER



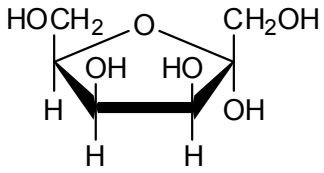




BOTH
(equally)

NEITHER

2. (23 pts) D-tagatose, a ketohexose, is a naturally occurring sucrose substitute used in European diet soft drinks. One of its cyclic, furanose (5-membered ring) anomers is shown at right.



D-tagatose

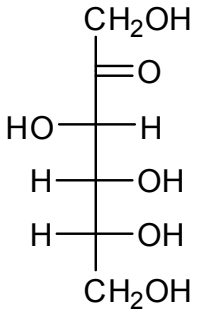
   a. This furanose form equilibrates with an acyclic form. Draw the acyclic form of D-tagatose as a Fischer projection in the box on the lower right.

   b. This acyclic form also equilibrates with two pyranose (6-membered ring) anomers. Draw one of those two anomers in their most stable chair conformations in the box below.

one pyranose anomer of D-tagatose (drawn as its most stable chair conformer)

acyclic form of D-tagatose (Fischer projection)

   c. The Fischer projection for D-fructose is shown at right. Is D-fructose an epimer of D-tagatose?



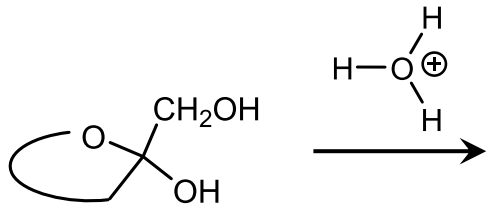
D-fructose

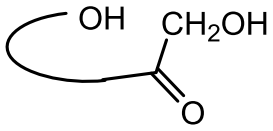
YES *or* **NO** ?

(circle one)

d. In the box below, draw an acid-catalyzed mechanism (using "electron pushing") for the formation of acyclic D-tagatose from the 5-membered ring form. Draw each molecule and mechanistic step explicitly; don't cheat by combining multiple processes in a single step, by taking shortcuts. For this problem, feel free to illustrate both open and ring-closed forms of tagatose as cartoon loops; you do not need to draw the sugar structure.

Mechanism:

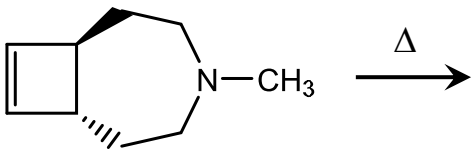


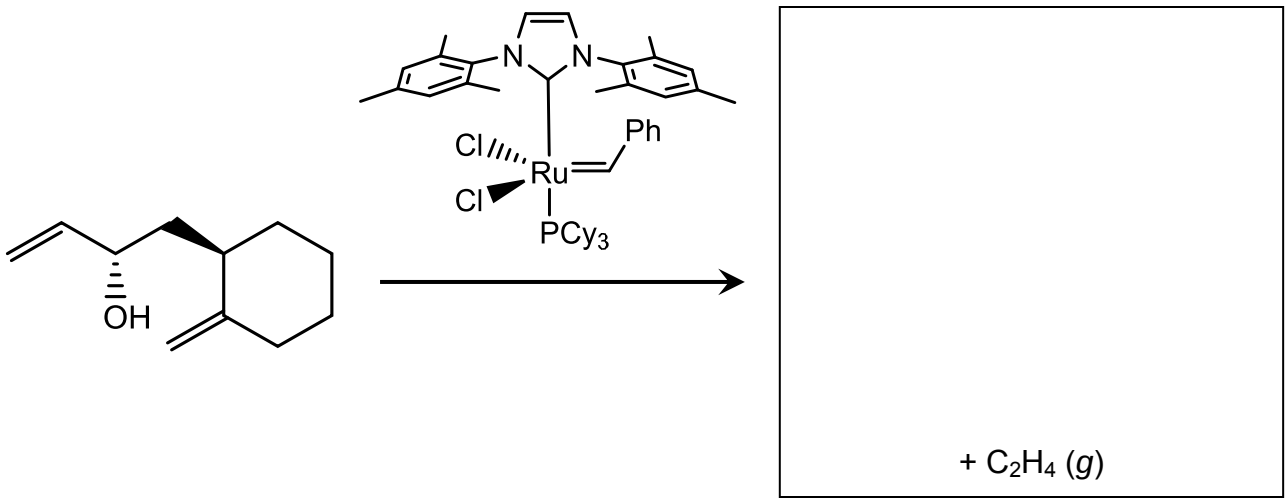


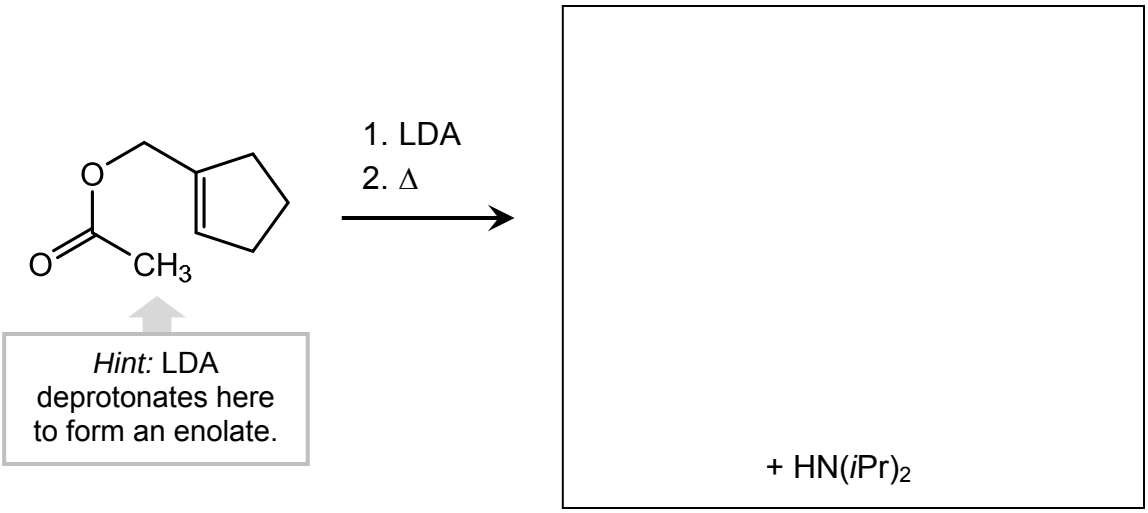
e. What is the timescale of this ring opening? Does it take place spontaneously over

minutes? **weeks?** *or* **decades?** *(Circle one.)*

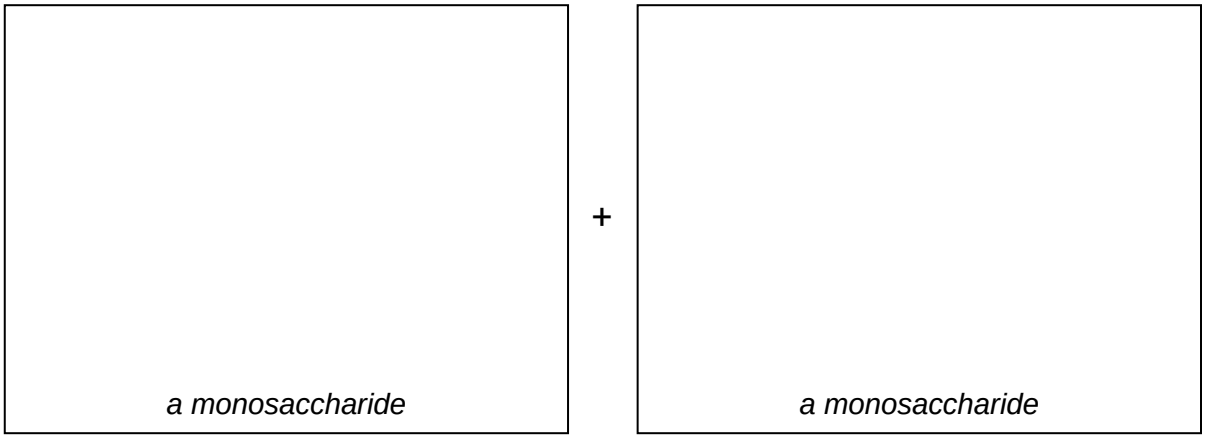
3. (23 pts) For each of the reactions below, fill in the empty box corresponding to reactants or product. Give only one answer in each box. For reactions that you expect to yield multiple products, draw one major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".

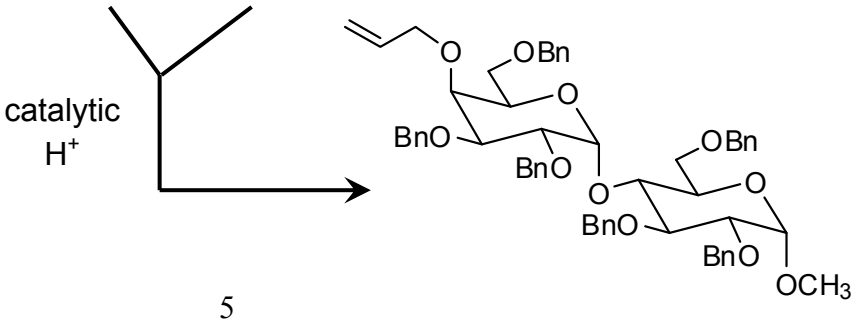




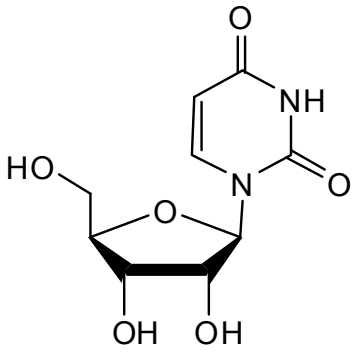


Hint: LDA deprotonates here to form an enolate.





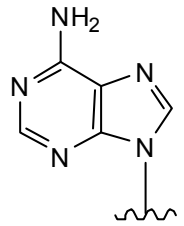
4. (12 pts)
   a. For the nucleoside below on the left:
      - **Label the 3'- and 5'-carbons** with their numbers;
      - Circle whether the nucleoside is a component of DNA or RNA;
      - Circle the base on the right that the base is normally paired within a double helix.

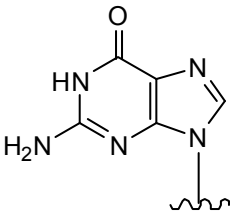


component of

DNA *or* **RNA** ?

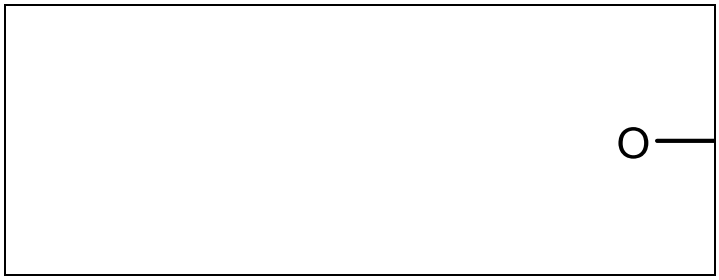
(circle one)



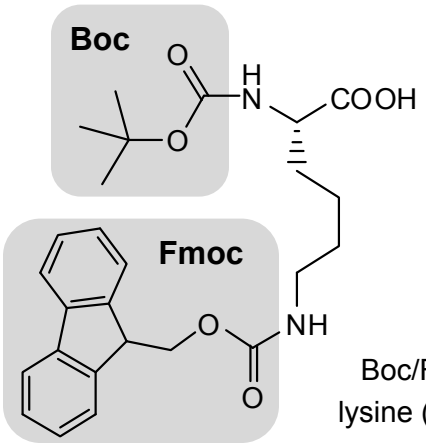


which of these bases pairs with base on the left?
(circle one)

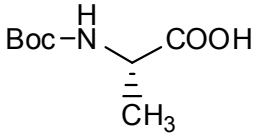
   b. In adenosine triphosphate (ATP), the 5'-carbon bears a phosphoanhydride triphosphate. Draw this group.



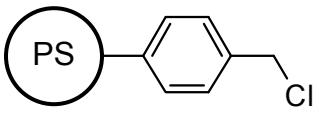
5. (26 pts) Using the starting materials shown below—chloromethylated polystyrene resin, and two *t*-butoxycarbonyl (Boc)-protected amino acids—propose a multistep, solid-phase synthesis of the dipeptide (H_2N)-**Ala-Lys-**(COOH). Apart from the Boc protecting group, the other amine of the lysine is protected with a fluorenylmethoxycarbonyl (Fmoc) group, which can be removed under basic conditions (*e.g*, w/ piperidine) to reveal the amine. *Answer on the next page.*



Boc/Fmoc-protected lysine ("Boc/Fmoc-Lys")



Boc-protected alanine ("Boc-Ala")



chloromethylated polystyrene

Feel free to use names and symbols instead of structures in your synthesis scheme.

Solid-phase synthesis of (H_2N)-Ala-Lys-(COOH):

What is the structure of (H_2N)-**Ala-Lys-**(COOH) at its isoelectric point (pI)?

What would the pI of this dipeptide be?

pI =

Structure of (H_2N)-Ala-Lys-(COOH) at pI:

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

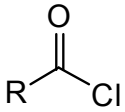
1. $NaNO_2$
   HCl
2. CuCN *or*
   H_3PO_2 *or*
   CuX *or*
   H_3O^+

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

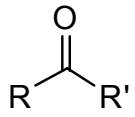
RLi

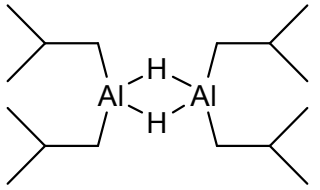
R_2CuLi

$Na_2Cr_2O_7$
H_2SO_4

$LiAlH(OtBu)_3$

1. Ag_2O
   NH_3
2. H_3O^+

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



(DIBAL-H)

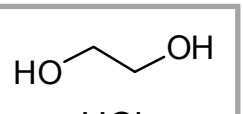
$Bu_4N^+F^-$

$PhCH_2Br$
Ag_2O

1. $LiAlH_4$
2. H_2O

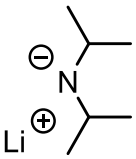
$(COCl)_2$

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



HCl

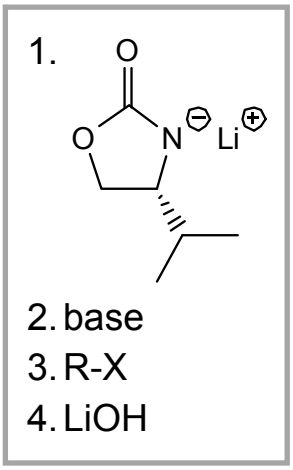
$NaNH_2$

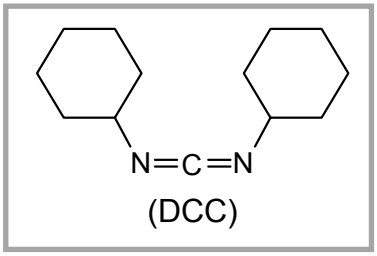


(LDA)

$SOCl_2$
(& pyridine,
usually)

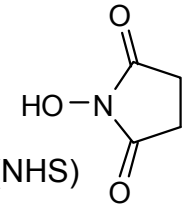
1. $NaBH_4$
2. H_2O





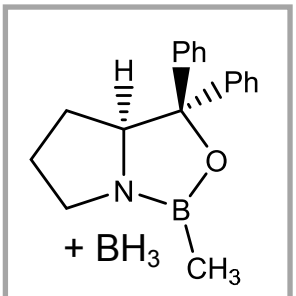
(DCC)

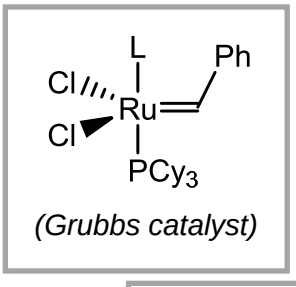
$CHCl_3$
$KOtBu$



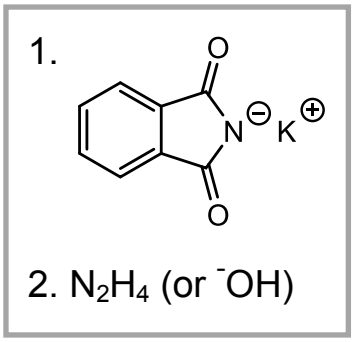
(NHS)

1. CH_3I
   (excess)
2. Ag_2O
   H_2O



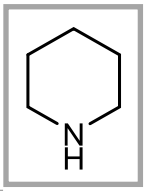


(Grubbs catalyst)



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

1. $PhNCS$
2. H^+
(Edman degradation)



1. NaN_3
2. PPh_3
   H_2O

CH_2I_2
$Zn(Cu)$

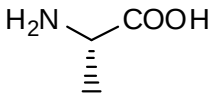
$Pd(PPh_3)_4$
NaOH

HF

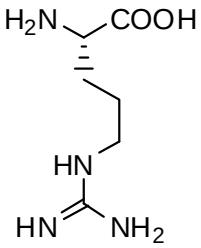
CF_3COOH

$Pd(OAc)_2$
PPh_3, NEt_3

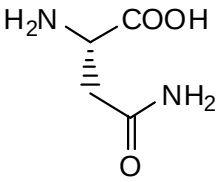
Exam 4 Chart of Amino Acids
(in Alphabetical Order)



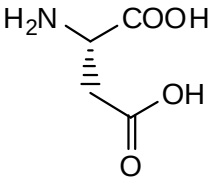
alanine
(Ala, A)



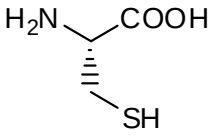
arginine
(Arg, R)



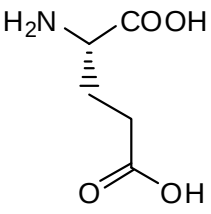
asparagine
(Asn, N)



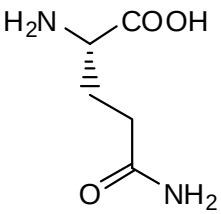
aspartic acid
(Asp, D)



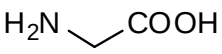
cysteine
(Cys, C)



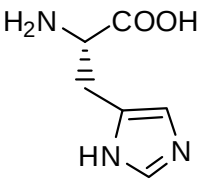
glutamic acid
(Glu, E)



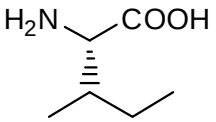
glutamine
(Gln, Q)



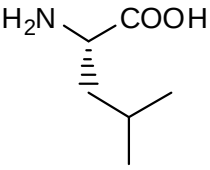
glycine
(Gly, G)



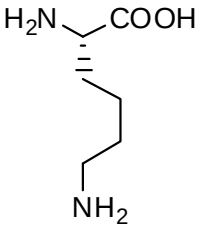
histidine
(His, H)



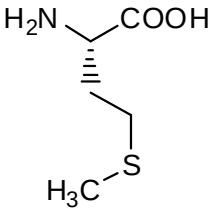
isoleucine
(Ile, I)



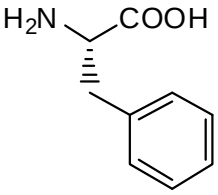
leucine
(Leu, L)



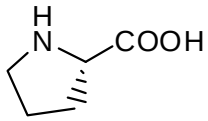
lysine
(Lys, K)



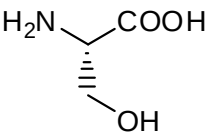
methionine
(Met, M)



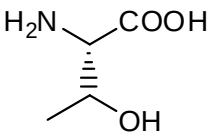
phenylalanine
(Phe, F)



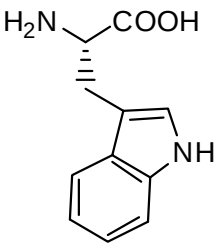
proline
(Pro, P)



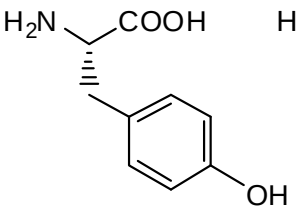
serine
(Ser, S)



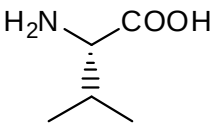
threonine
(Thr, T)



tryptophan
(Trp, W)

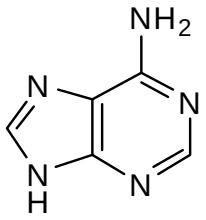


tyrosine
(Tyr, Y)



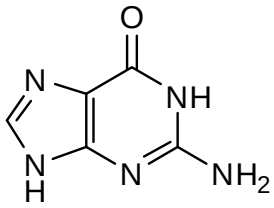
valine
(Val, V)

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

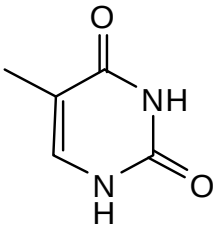


adenine
(A)

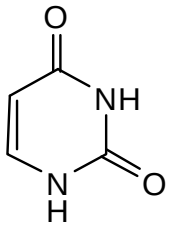
cytosine
(C)



guanine
(G)



thymine
(T)



uracil
(U)

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.