

CHEMISTRY 3A SPRING 2013

EXAM 2

APRIL 4, 2013

Answer
Key.

NAME _____

SECTION AND/OR TA IF YOU ARE IN THE LABORATORY COURSE: _____

STUDENT ID: _____

- You will have 2 hours in which to work.
- BE NEAT! Non-legible structure drawings will not be graded.
- All pages of the exam must be turned in.
- No calculators
- Molecular models may be used

Page	Points (Maximum)	Points (Obtained)
2	30	
3	28	
4	44	
5	20	
6	25	
7	18	
8	22	
9	13	
<i>Total</i>	<i>200</i>	

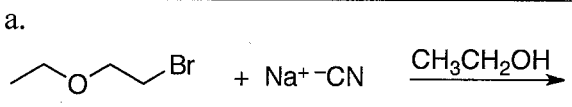
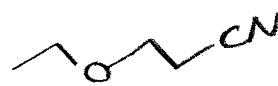
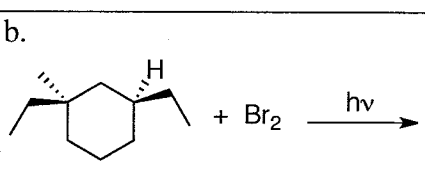
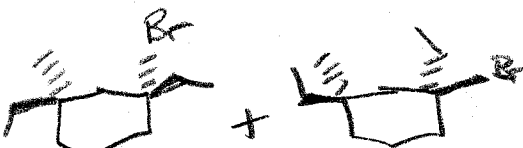
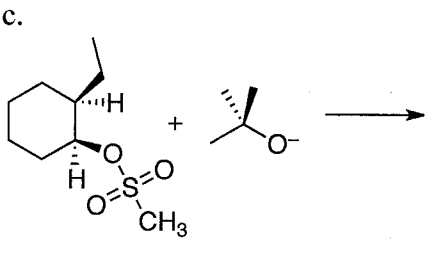
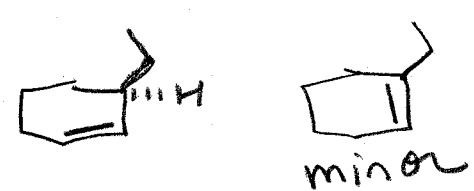
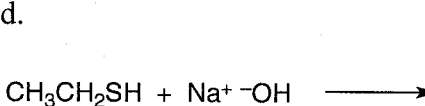
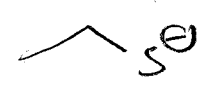
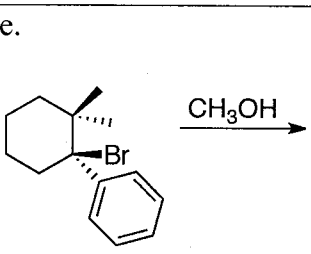
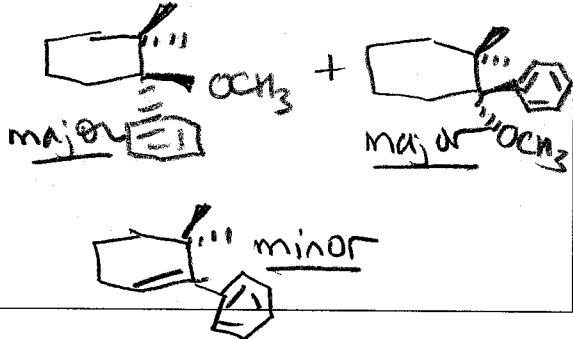
1. (30 points) For each reaction:

(i) Draw the major and minor organic products. Write NR if you think there will be no reaction.

(ii) Label each product you draw as major or minor.

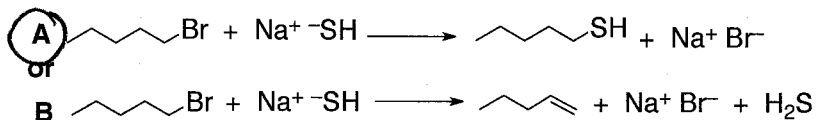
(iii) Indicate the stereochemistry of the products.

(iv) Identify the type of mechanism(s): S_N2, S_N1, E1, E2, radical halogenation, or Brønsted acid/base.

	Product(s)	Mechanism Type
a. 		S _N 2
b. 		radical halogenation
c. 		E2
d. 		Acid/ Base
e. 		S _N 1 E1

2. (28 points) Which reaction in the following pairs of reactions would you expect to go faster? It is possible that both reactions have the same rate. Give brief explanations in the boxes provided.

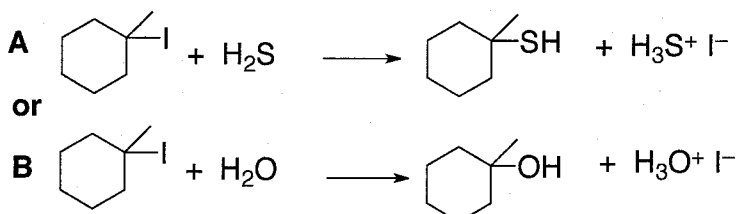
a.



Explanation:

A is faster because $-SH$ is a great nucleophile & a weak base, Unhindered 1^o substrate. Therefore, S_N2 faster

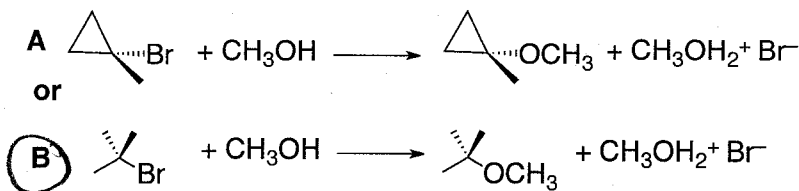
b.



Explanation:

Same rate
 These are S_N1 rxns
 The rate of the rxn only depends on alkyl iodide, Rate does not depend on nucleophile.

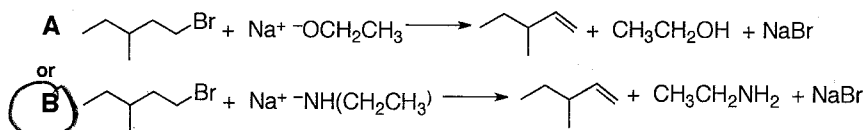
c.



Explanation:

B is faster. In A the transition state & carbocation intermediate are destabilized by bond angle strain. It is difficult for the 3-membered ring w/ 60° angles to become sp^2 hybridized.

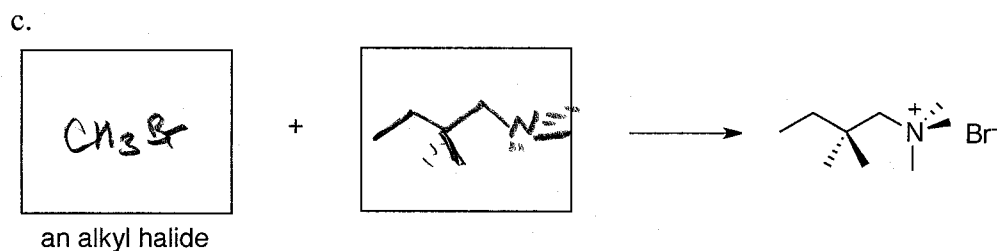
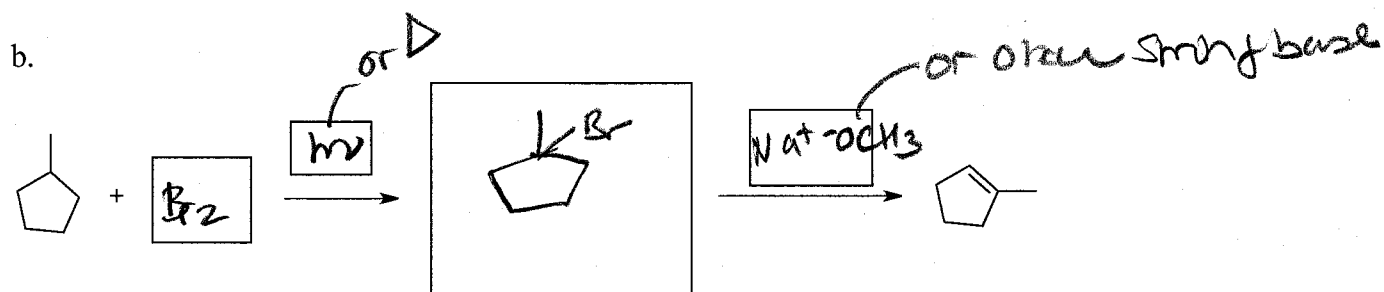
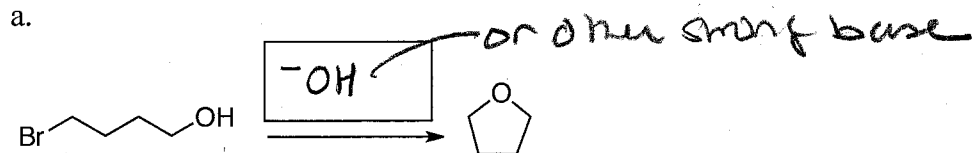
d.



Explanation

B is faster. This is an $E2$ rxn & $-NH(CH_2CH_3)$ is a stronger base than $-OCH_2CH_3$

3. (28 points) Fill in the boxes in the following reactions to yield the indicated products in the highest yield with the fewest number of steps. Note that only the organic products have been drawn.



4. (16 points) Give the mechanism(s) that are true for the following statements. Choose from S_N2 , S_N1 , E1, E2, and/or radical halogenation.

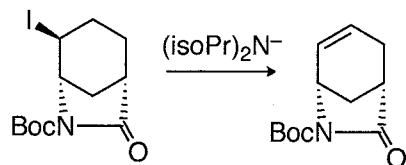
a. These reaction mechanisms involve carbocation intermediates $S_N1, E1$

b. These reactions follow a second order rate equation $S_N2, E2$

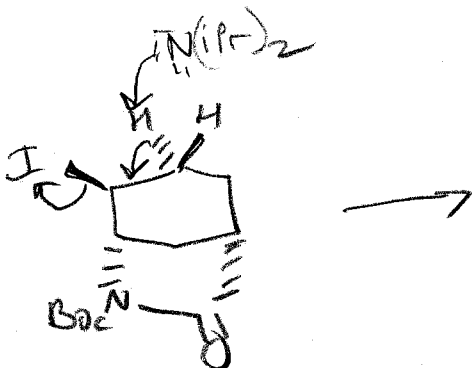
c. Alkyl iodides react faster than alkyl bromides in reactions that proceed by these mechanisms. $S_N1, E1, E2, S_N2$

d. These reactions proceed through propagation steps. radical halogenation

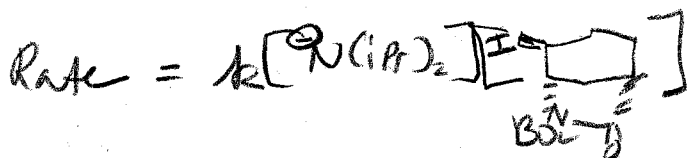
5. (20 points) Tamiflu is a medication used to prevent and treat flu. A step in the synthesis of Tamiflu is shown below.



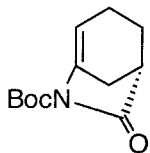
a. Draw the mechanism of this reaction using arrows to represent electron flow.



b. Write the rate equation for this reaction.



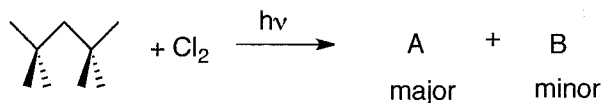
c. Why is the alkene shown below not a product of this reaction?



Three reasons

- ① No anti planar H's
- ② large base favors Hofmann elimination
- ③ Ring strain from double bond at bridgehead position

6. (37 points) Radical chlorination of $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_3$ gives a mixture of monochlorinated alkanes in a 2:1 ratio. Remember that the relative reactivity of $3^\circ:2^\circ:1^\circ$ C-H bonds is 5:4:1.



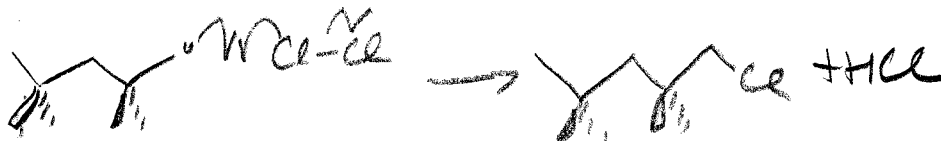
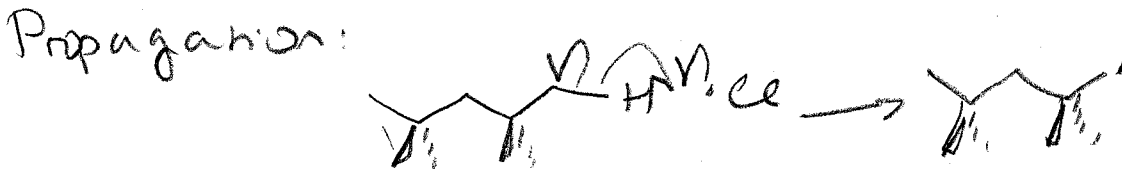
a. Is the observed product ratio consistent with the relative reactivity of 3° , 2° , and 1° C-H bonds? Show a calculation that justifies your answer.

$$\begin{array}{l}
 10\text{H} = 18\text{H's} \times 1 = 18 \\
 20\text{H} = 2\text{H's} \times 2 = 4
 \end{array}$$
 approximate 2:1 ratio

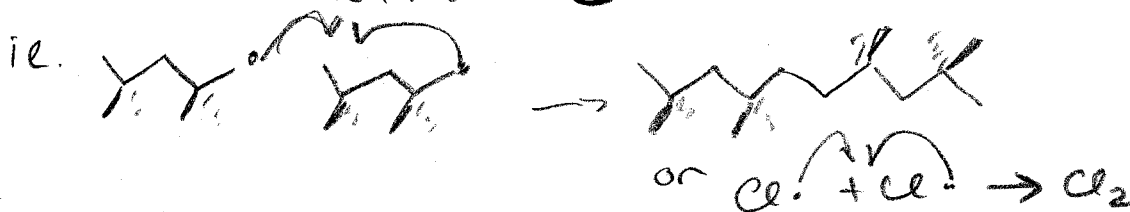
b. What is the major product of chlorination?



c. Draw the mechanism of the formation of the major product of chlorination using arrows to show electron flow.



Termination: Any reaction that does not form a radical

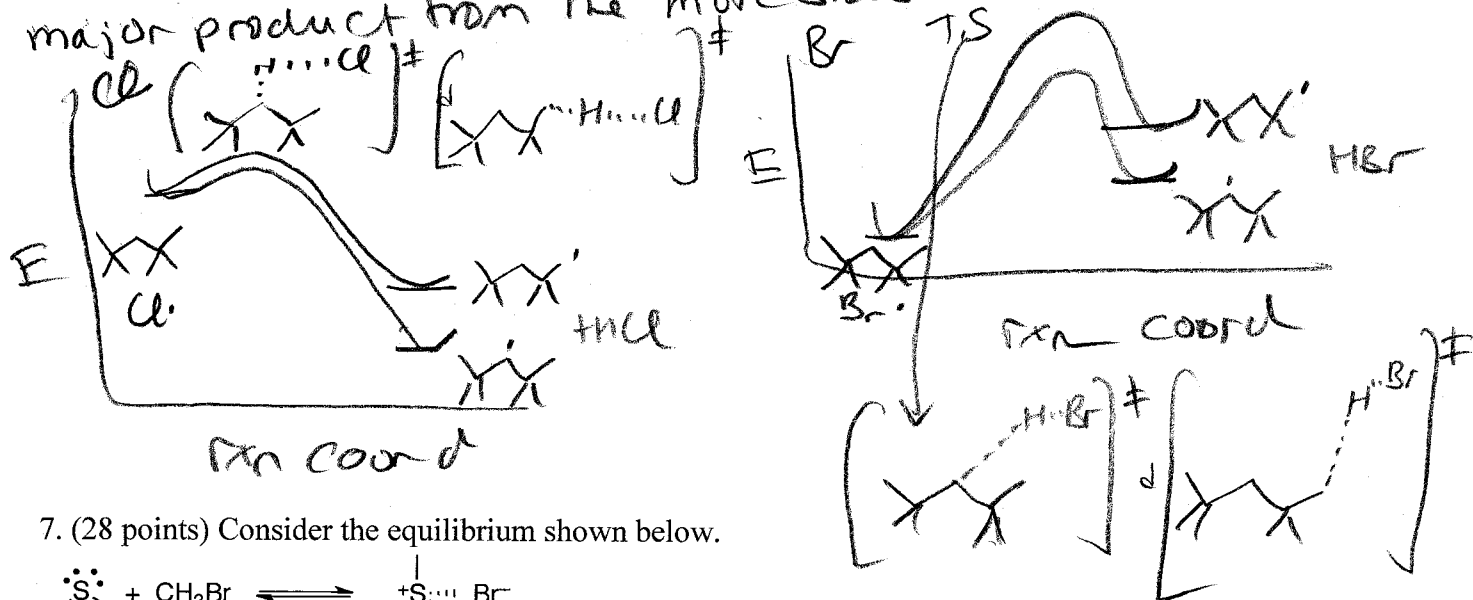


d. If this reaction is performed with Br₂ instead of Cl₂, then the major product is structure **B** with Br substituted for Cl. Explain why a different major product is observed with Br₂. Include in your answer a discussion of the Hammond postulate and the transition state structures involved in these reactions. The table lists some BDE's (bond dissociation energies) for your reference.

Bond	BDE (kcal/mol)
HCl	103
HBr	87
Br ₂	46
Cl ₂	58
1° C-H	101
2° C-H	98

The first step of propagation determines which C-H bond is halogenated. This step is endothermic for Br₂ & exothermic for Cl₂. The Hammond postulate states that the TS for exothermic will look more like reactants, TS for endothermic will look more like products.

Therefore, T.S. for Cl₂ will look more like alkane + HCl, T.S. for Br₂ will look more like radicals. Therefore, there will be a larger energy difference between 1° C-H & 2° C-H rxns for Br₂ than Cl₂ & Br₂ will therefore yield the major product from the more stable radical (B)



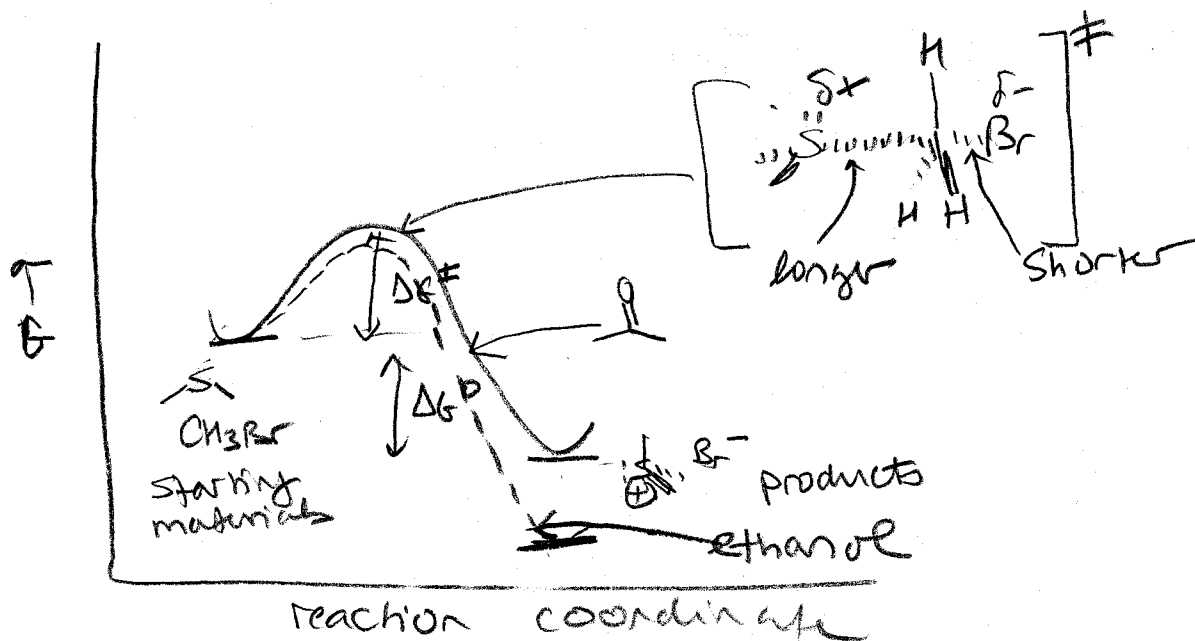
7. (28 points) Consider the equilibrium shown below.



a) Draw the mechanism for this reaction.



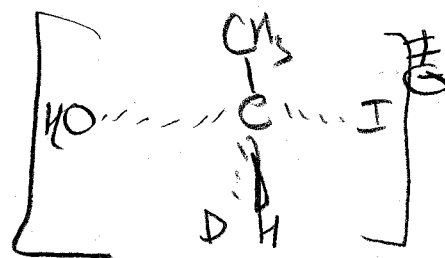
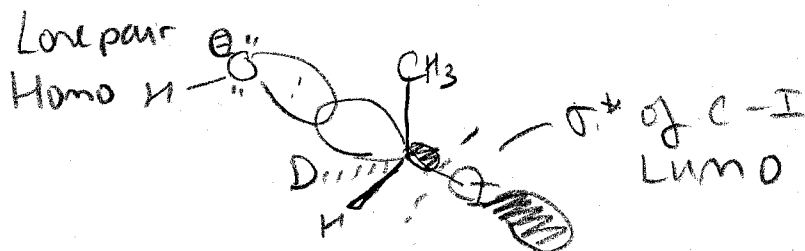
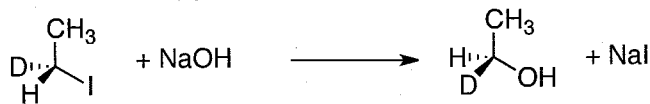
b) Draw a reaction coordinate diagram for this reaction. Label the axes, starting materials, products, ΔG° , ΔG^\ddagger , intermediates, and transition states. Include a drawing of the transition state structure.



c) The *equilibrium* of this reaction lies farther to the right in ethanol than in acetone. Explain this observation. As part of your explanation, annotate the diagram you drew in part b to include reactions in both solvents.

The products of this reaction are charged, the starting materials are neutral. The TS is partially charged. Therefore, the more polar EtOH will stabilize the products through solvation. The neutral starting materials will not be very affected by solvation. Therefore, the equilibrium will lie further to the right in the more polar solvent EtOH. (The T.S. will also be stabilized by increased solvation in EtOH, but by less than products)

8. (13 points) The S_N2 mechanism is stereospecific and proceeds with inversion of configuration. An example of a reaction that proceeds by an S_N2 mechanism is shown below. Explain why the S_N2 mechanism proceeds with inversion of configuration. Include in your explanation a discussion of and labeled drawings of the orbitals involved in this reaction.



The lone pair of the HO^- initiates the reaction by donating e^- into σ^* of C-I bond. σ^* orbital is larger away from the C-I bond (the back of the bond). The back of the C-I bond is also less sterically hindered than the front of the C-I bond. Approach from the front of the bond would yield equal interactions w/ both signs of σ^* orbital & these would cancel out leading to no interaction. The C-I bond breaks at the same time as the C-O bond forms. The T.S. is a trigonal bipyramidal structure & the molecule undergoes an umbrella flip during this reaction. Together these reasons cause inversion of configuration.

ChemGlobe - Periodic table of elements

<http://periodictable.tsx.org>

										<table border="1"> <tr> <td>Atomic number</td> <td>43</td> <td>(98.91)</td> <td>Atomic mass (mean relative)</td> </tr> <tr> <td>Symbol</td> <td colspan="2">Tc</td> <td></td> </tr> <tr> <td>Melting point (°C)</td> <td>2540</td> <td>± 11</td> <td>Density (g/cm³, for gases (g/l) (0°C, 1013mbar)</td> </tr> <tr> <td>Boiling point (°C)</td> <td>2930</td> <td>± 19</td> <td>Electronegativity</td> </tr> <tr> <td></td> <td colspan="3" style="text-align: center;">Radioactive</td> </tr> </table>										Atomic number	43	(98.91)	Atomic mass (mean relative)	Symbol	Tc			Melting point (°C)	2540	± 11	Density (g/cm ³ , for gases (g/l) (0°C, 1013mbar)	Boiling point (°C)	2930	± 19	Electronegativity		Radioactive												
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1.008	4.003											2.78	2.25	2.25	2.25	2.25	2.25																																
1.00794	4.00260											2.688	2.809	30.97	32.06	35.45	39.95																																
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39.10	40.08	44.96	47.88	50.94	52.00	54.94	55.85	58.93	58.71	63.55	65.38	69.72	72.59	74.91	78.96	79.90	83.80																																
39.0983	40.078	44.9559122	47.8828	50.9415	52.0038	54.937025	55.845	58.932894	58.70643	63.546	65.38	69.723	72.591	74.901585	78.961848	79.904	83.80																																
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85.47	87.62	88.91	91.22	91.22	95.94	98.91	101.07	102.91	106.42	107.87	112.41	114.82	118.69	121.76	127.60	126.90	131.29																																
85.4678	87.62	88.905842	91.224	91.224	95.94	98.906251	101.07	102.9055	106.4196	107.8642	112.411	114.818	118.689	121.757	127.603	126.905	131.294																																
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132.91	137.33	174.97	178.49	180.95	183.85	186.21	190.20	192.22	195.08	196.97	200.59	204.38	207.20	208.98	(209)	(210)	(222)																																
132.90545196	137.327	174.967	178.489	180.948	183.848	186.207	190.199	192.222	195.084	196.966569	200.59244	204.377	207.19	208.980389	(209)	(210)	(222)																																
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(223)	(226)	(260)	(261)	(262)	(263)	(264)	(265)	(266)	(267)	(268)	(269)	(270)	(271)	(272)	(273)	(274)	(275)																																
(223)	(226)	(260)	(261)	(262)	(263)	(264)	(265)	(266)	(267)	(268)	(269)	(270)	(271)	(272)	(273)	(274)	(275)																																
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Lanthanoids	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																																			
	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	173.04																																			
	138.90547	140.116	140.90766	144.242	(145)	150.358	151.964	157.254	158.92535	162.5021	164.93033	167.25977	168.93032	173.045																																			
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Actinoids	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																																			
	227.03	232.04	231.04	238.03	(237.04)	(244)	(243)	(247)	(247)	(251)	(254)	(257)	(258)	(259)																																			
	227.03541	232.0377	231.03626	238.02891	(237.04371)	(244)	(243)	(247)	(247)	(251)	(254)	(257)	(258)	(259)																																			

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