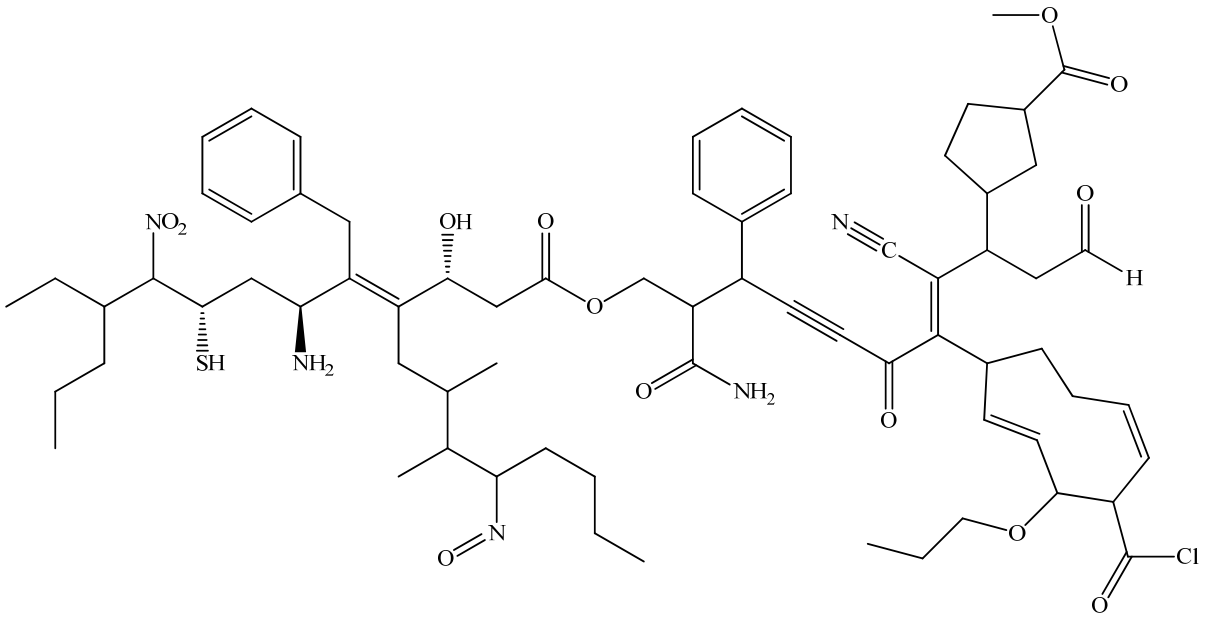
Chem 201 Midterm
Spring, 2018
Beauchamp Name _____

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)	30	
7. 2D Lewis Structures (1, large)	20	
8. Functional Groups, Names or Types of Isomers or Special Types of Carbons and Substituents, Degrees of Unsaturation	25	
9. Forces of Interaction and Physical Properties	20	
10. Properties of Atoms, (ionization potential, Z_{eff}, radii, electronegativity), Logic Arguments of Organic Chemistry (inductive, resonance, steric)	30	
Total	258	

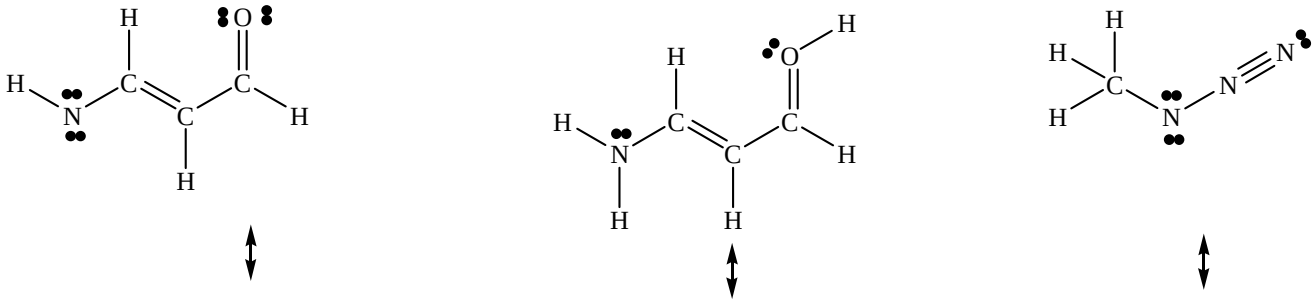
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron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

I have no special talent. I am only passionately curious. Albert Einstein

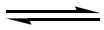
1. Provide an acceptable name for the following molecule. Only specify R and S where shown as 3D. (30 pts)



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. (18 pts)



3. Draw all possible chair conformations of trans-1- mercapto-2-phenyllcyclohexane. The axial energy of the thiol group is 1.2 kcal/mole and axial energy of phenyl is 2.9 kcal/mole. The gauche energy of thiol/phenyl is 1.1 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 most stable conformation using the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any gauche interactions of the substituents shown in your Newman projection. What is the ratio of the two conformations at equilibrium? Show your work. 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. (30 pts)

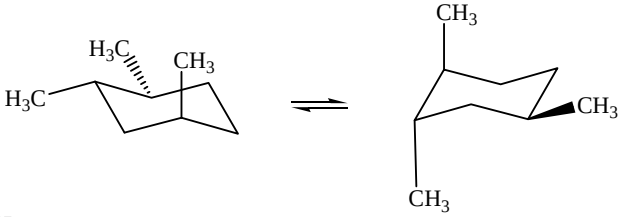


conformation 1 conformation 2

b. Newman projection ($C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$) – most stable, point out any gauche interactions with the substituent(s). (5 pts)

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

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 C1→C2 bond of 1-bromo-1-phenyl-2,2-dimethylbutane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table 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.

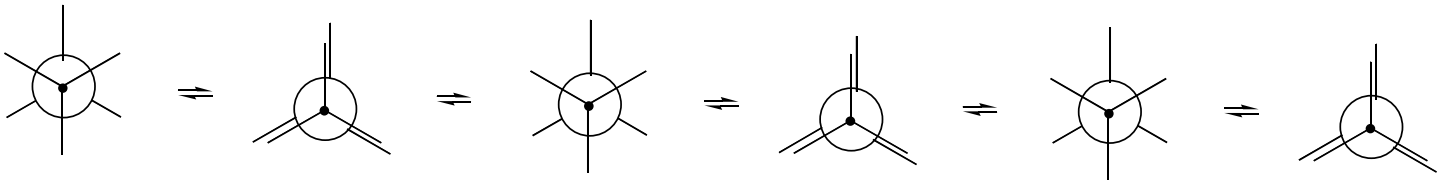
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.6	3.0	1.5	1.1
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1	1.6
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9	3.3
Ph	0.2	1.4	1.5	2.1	3.9	2.3	1.9
Br	0.1	1.0	1.1	1.6	3.3	1.9	1.1

$\Delta G \approx \Delta H$

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

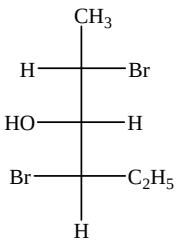
Newman projections:

lowest PE

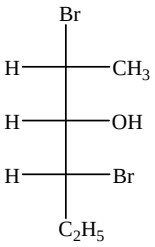


K_{eq} calculation

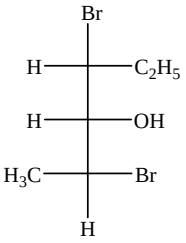
5. Use the following set of Fischer projections to answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify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



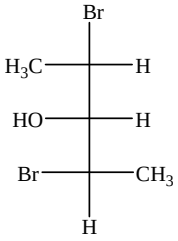
(3 pts) A



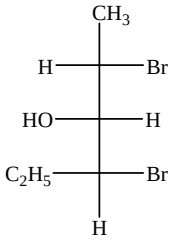
B



C



D



E

(17 pts)

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

b. Which are meso? A B C D E

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

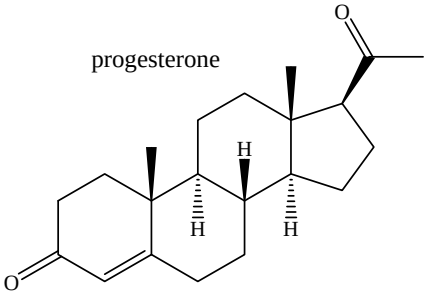
f. Which pairs are diastereomers? AB AC AD AE BC BD BE CD CE DE

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 2,4-dibromohexan-3-ol as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)

i. Progesterone is a crucial steroid in metabolism and various corticosteroids and sex hormones are made from it. It prepares the uterus for implantation and inhibits lactation while a women is pregnant. However, men need it too. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)

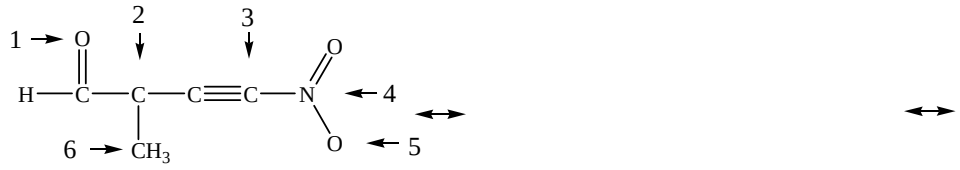
progesterone



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)

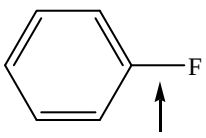
(10 pts)

Use the given (first) Lewis structure to answer this part. (10 pts)

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

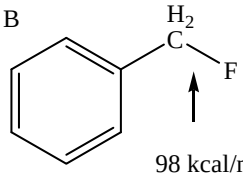
Explain the different C-F bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of the fluorine atom in A and B? (4 pts)

A



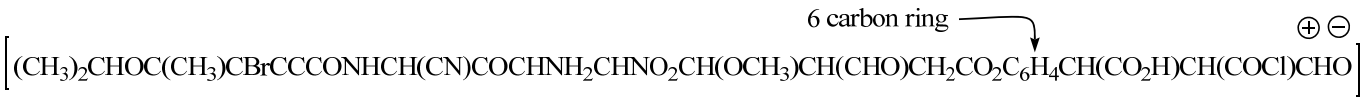
126 kcal/mole

B



98 kcal/mole

7. Draw an acceptable Lewis structure (2D) for the following structure. Show <u>all</u> 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)

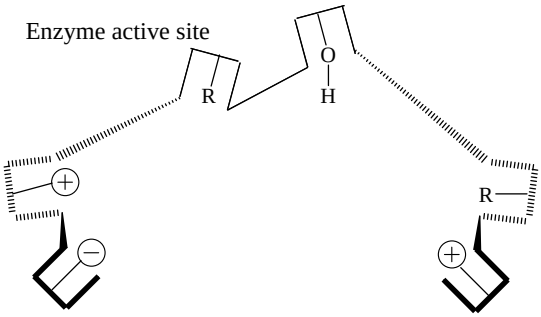


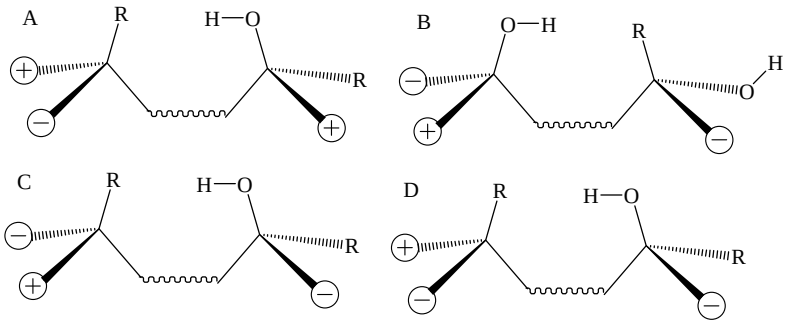
8. Draw an example molecule that has the indicated functional groups. Name each functional group. (25 pts)

functional groups: carboxylic acid, anhydride, thiol, 3^o amide, 2^o amine, alcohol, ether, alkene, alkyne, cyclic alkane, bromo, aromatic, acid chloride, ester, aldehyde, ketone

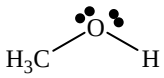
Use the given molecular formula to calculate the degree of unsaturation. Show work. $C_{21}H_{24}BrClFN_3O_5$, (5 pts)

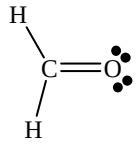
9. a. The active site of an important liver enzyme has just been discovered. Several key regions are shown in the enzyme active site, just below. As an employee of Bronco Pharmaceutical, you are trying to design an inhibitor molecule that will strongly bind to the key regions of the active site so that 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 choice will work best. (10 pts)

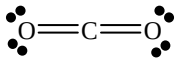




b. Methanol, methanal and carbon dioxide become gases at -78°C, -20°C and +65°C. Match each temperature with the correct compound and provide an explanation for you answer. (10 pts)



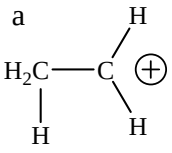




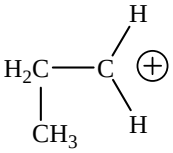
10. Logic arguments of organic and biochemistry

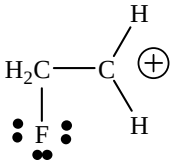
a. The first molecule in each row is a reference point. Explain if the indicated substitution will be stabilizing, destabilizing or have no effect relative to the reference structure. Provide an explanation for your answer. (10 pts)

a

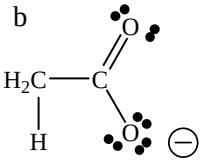


ref. structure

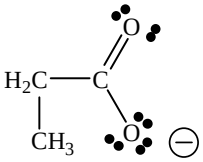


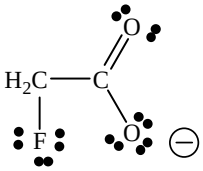


b



ref. structure





b. Which atom has the higher first ionization potential and why? (O or P) (20 pts, 5 pts each)

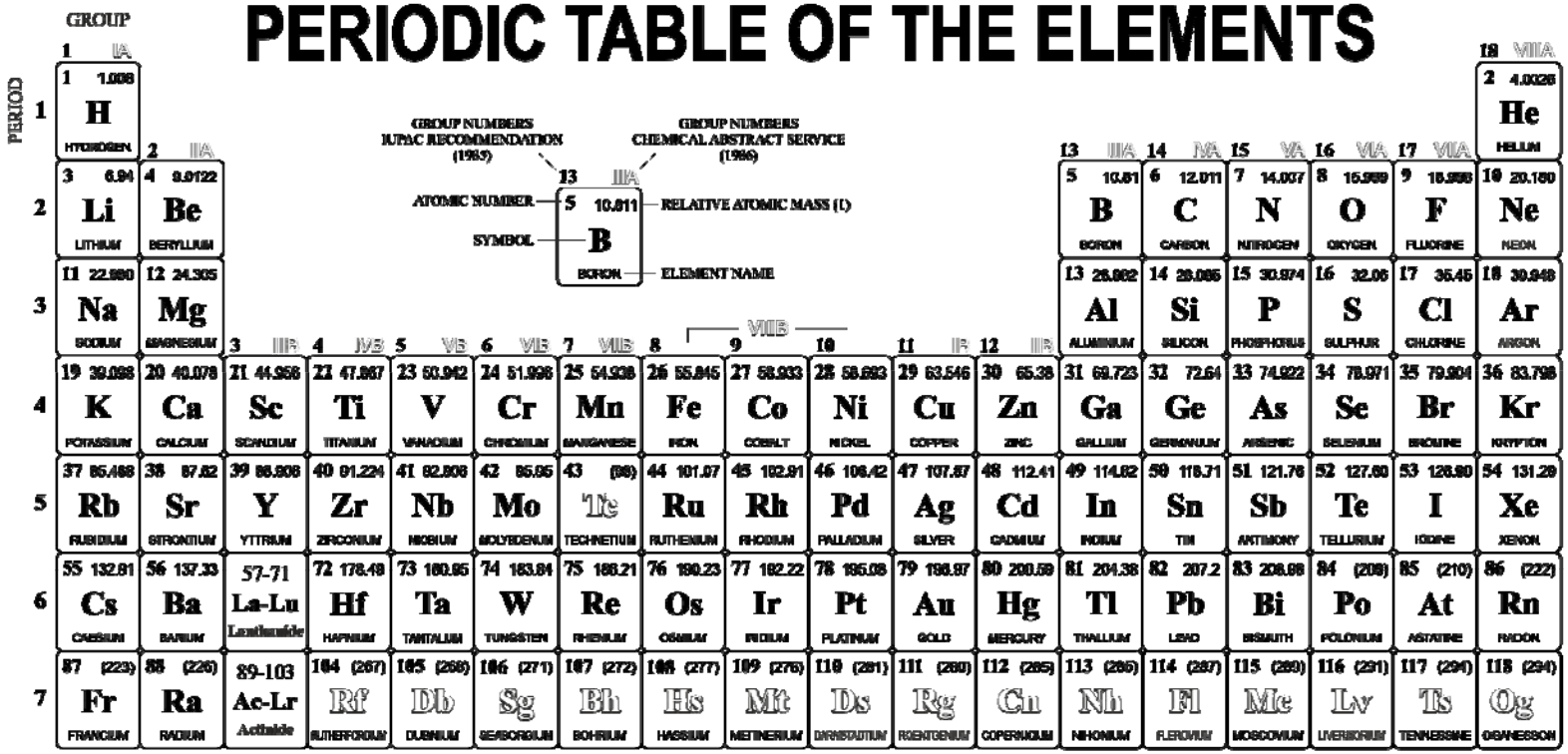
c. Which neutral atom has the larger atomic radius and why? (S or P)

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

e. Which cation has the larger radius and why? (Be^{+2} or B^{+3})

Change is the end result of all learning. Leo Buscaglia

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

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